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# INTERNAL FRICTION OF THE IODINE CHLORIDE - ACETAMIDE AND IODINE CHLORIDE - BENZAMIDE SYSTEMS.

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Our previous research has established the ability of the amides of organic acids to form coordination compounds with iodine chloride[1,2]. A compound of this sort, $C_6H_5CONH_2 \cdot ICl$, for example, was discovered by us by the method of thermal analysis, by the cryoscopy of this system in a nitrobenzene solution, and by a study of the solubility of benzamide in a solution of iodine chloride in $C_6H_5NO_2$. Electrolysis and ion-transfer experiments have shown that benzamide and iodine constitute the cation of the $C_6H_5CONH_2 \cdot ICl$ coordination compound, the anion being chlorine, which may be expressed by this formula:

$$[C_6H_5CONH_2 \cdot I]Cl^{[2]}.$$

A study of the $CH_3CONH_2$ - ICl system led us to the same conclusion concerning the composition and structure of the coordination compound, in this case the conclusion regarding the existence of the $CH_3CONH_2 \cdot ICl$ compound being drawn solely on the basis of cryoscopy of the $CH_3CONH_2$ - ICl system in nitrobenzene solutions and a study of ion transfer[1].

Endeavors to investigate this system by the method of thermal analysis were unsuccessful, as it was impossible in most tests to effect crystallization of this system in the central region of the concentration range: chilling yielded a hyaline mass, which did not crystallize when the usual methods to effect this were employed. At the same time we observed that the viscosity of the $CH_3CONH_2$ - ICl system rose considerably (even in the central region of the concentration range), which may have been one of the factors that interfered with crystallization.

In view of these results of our investigation of the $CH_3CONH_2$ - ICl and $C_6H_5CONH_2$ - ICl systems, we resolved to supplement them by measuring the internal friction.

As we know, viscosimetry is one of the most sensitive methods of physico-chemical analysis, enabling one to establish the presence or absence of chemical reaction between the components of a system, as well as the composition of new compounds formed within the system, being close to thermal analysis in this respect (in point of sensitivity).

Moreover, a fairly large array of facts, established chiefly by N.S.Kurnakov and his co-workers, is known, viz.: whereas thermal analysis indicates the formation of new compounds in the given system, these compounds are not manifested on the isotherms of internal friction. Facts supporting the converse conclusion are also known.

Likewise, it has often been observed[3,4], that when several new compounds have been formed in a binary system, only some of them, the most stable ones, are shown on the viscosity diagram.

In undertaking the measurement of internal friction in the $CH_3CONH_2$ - ICl and $C_6H_5CONH_2$ - ICl systems, we proposed to expand the investigation of these systems to ascertain the nature of their chemical reactions, and also to make a comparison of various methods of physico-chemical analysis as applied to these systems.

## EXPERIMENTAL

The initial substances — iodine chloride, acetamide, and benzamide — were prepared or purified as described in our previous reports[1,2].

The freezing points of these substances were as follows; for ICl: 27.15°; for $CH_3CONH_2$: 81.5°; and for $C_6H_5CONH_2$: 127.8°. These values agree with the data given in the literature for well-purified preparations.

The test solutions were prepared directly in the viscosimeter, adding weighed batches of acetamide or benzamide to a weighed amount of ICl.

Viscosity was measured in the viscosimeter described in the paper by I.L. Katsnelson and A.V.Bernshtein[5]. We made some changes in the design of this instrument. The viscosimeter is illustrated schematically in Fig. 1.

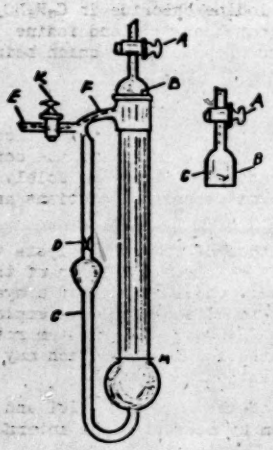


Fig. 1. Viscosimeter.

Fused ICl was poured into the right-hand arm of the viscosimeter up to the mark M on the bulb, after which the viscosimeter was closed with the ground-in cap B, fitted with stopcock A, which remained open at the start. The stopcock was turned so that the opening O did not coincide with the axis of tube F. Calcium-chloride tubes, filled with anhydrous calcium chloride, were placed on the top stopcock A and the left stopcock E, and were connected to the stopcocks by rubber sleeves.

The viscosimeter was filled to above the mark D with a solution for viscosity measurement, using the vacuum produced by a low-pressure water-jet pump. A device was inserted between stopcock K and the pump to enable us to break off the process of filling the viscosimeter quickly; this line also had a valve to prevent water from being drawn into the system, and a drier to absorb any moisture that might enter the viscosimeter while a vacuum was being set up within it.

After the left arm had been filled with solution to the mark D, stopcocks A and K were closed, and cap B was turned so that the opening O was in line with the interior of tube F; this caused the solution to flow from the left arm into the right. Thus the solution did not come in contact with the outside air even during this transfer.

The viscosity was measured after the viscosimeter had been kept in a thermostat for 15 to 20 minutes at the measurement temperature of C $\pm$ 0.10°.

Water was used as the standard liquid. The viscosity was calculated from

the formula:

$$\eta_p = \frac{t_p \cdot d_p}{t_0 \cdot d_0} \cdot \eta_0$$

where $\eta_0$, $d_0$, and $t_0$ are the viscosity, density, and discharge time, respectively, for water at the given temperature, and $\eta_p$, $d_p$ and $t_p$ are the corresponding quantities for the system under test. The absolute viscosity and specific gravity of water were taken from the Landolt tables (V, I, p 83, 73).

As the level of the liquid in the viscosimeter changed each time, depending upon the size of the batches of ICl and $CH_3CONH_2$ or $C_6H_5CONH_2$, the viscosimeter was graduated for the discharge rate of water at various levels. These figures were used to plot a graph showing the discharge time for water versus the height of the liquid level in the viscosimeter bulb, in millimeters.

Every time the viscosimeter was filled with the test solution, the height of the liquid level in the viscosimeter above the mark N was measured, and the water-discharge time for the given liquid level was taken from the graph to compute the viscosity.

The viscosity of the ICl - $CH_3CONH_2$ system was determined at the temperatures of 25, 35, and 45° for concentrations ranging from 100% ICl to 77.5 mol % $CH_3CONH_2$.

The ICl - $C_6H_5CONH_2$ system was investigated only at 50° throughout the concentration range from 100% ICl to 61 mol % benzamide. The peculiarities in the fusibility diagram of this system — the great difference between the melting points of the two components — did not allow us to measure the viscosity at temperatures below 40-50° in order to avoid the precipitation of the solid phase within the range of concentrations near the dystectic (50 mol % $C_6H_5CONH_2$). To cover a large concentration range (from 60 to 100 mol % $C_6H_5CONH_2$) we should have had to make the measurements at temperatures in excess of 100°, which might have involved the thermal dissociation of the iodine chloride [6].

TABLE 1

Viscosity of the $CH_3CONH_2$ — ICl system

| Molar % $CH_3CONH_2$ | Viscosity, centipoises | | |
|---|---|---|---|
| | 45° | 35° | 25° |
| 0 | 2.550 | 3.058 | 3.729 |
| 7.46 | 4.509 | 4.909 | 5.492 |
| 13.38 | 5.234 | 5 591 | 6.358 |
| 20.71 | 6.848 | 7.712 | 8.968 |
| 27.65 | 10.153 | 12.062 | 14.869 |
| 37.20 | 10.888 | 12.887 | 20.133 |
| 44.48 | 11.845 | 16.954 | 32.068 |
| 50.06 | 13.180 | 22.046 | 39.404 |
| 59.00 | 15.546 | 28.283 | 52.901 |
| 61.70 | 16.322 | - | - |
| 64.22 | 16.508 | 28.698 | - |
| 66.45 | 17.475 | 9.935 | 60.264 |
| 70.02 | 13.797 | 25.897 | - |
| 74.11 | 12.546 | 21.737 | 41.507 |
| 77.54 | 12.053 | 19.861 | - |

The results of our viscosity measurements are given in Table 1 and in Fig. 2 for the $CH_3CONH_2$ — ICl system, and in Table 2 and Fig. 3 for the $C_6H_5CONH_2$ — ICl system.

The specific gravity values of these systems required for the viscosity calculation were taken by interpolation from data previously obtained by us and cited in our preceding reports [1,2].

The measurements of the viscosity of the $CH_3CONH_2$ -- ICl system shown in Table 1 and Fig. 2 indicate that as the concentration of acetamide is increased, the viscosity of the system first rises for all three temperatures up to 66.5% $CH_3CONH_2$. As the concentration of acetamide is raised still higher, the viscosity

commences to drop.

Thus, there is a maxium near 66.6 mol % $CH_3CONH_2$ on all three viscosity isotherms, which does not shift with temperature and corresponds to a coordination compound with the composition of $2CH_3CONH_2 \cdot ICl$.

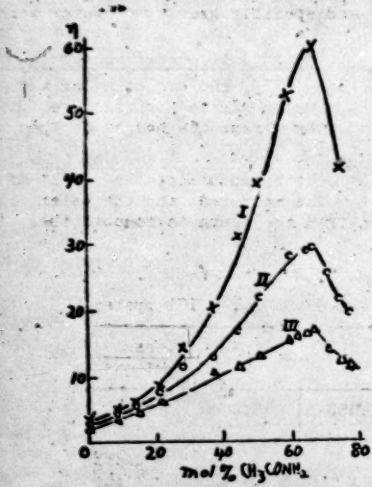


Fig. 2. Viscosity of the $CH_3CONH_2$ — ICl system.

I - viscosity at 25°;
II - viscosity at 35°;
III - viscosity at 45°.

This enables us to class the $CH_3CONH_2$ - ICl system as a so-called rational system, according to the Kurnakov classification, in which the compounds that are formed do not dissociate at the temperature of measurement.

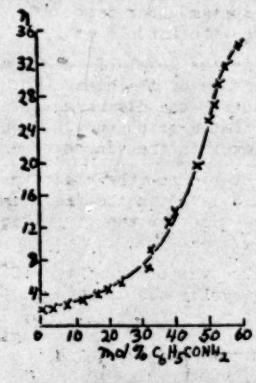


Fig. 3. Viscosity of the ICl — $C_6H_5CONH_2$ system.

Table 2

Viscosity of the $C_6H_5CONH_2$-ICl system

| Molar % $C_6H_5CONH_2$ | Viscosity centi-poises | Molar % of $C_6H_5CONH_2$ | Viscosity centi-poises |
|---|---|---|---|
| 0 | 2.255 | 38.87 | 12.585 |
| 2.75 | 2.412 | 41.52 | 13.812 |
| 6.95 | 2.749 | 47.84 | 19.494 |
| 11.47 | 2.287 | 51.05 | 24.819 |
| 15.69 | 4.017 | 55.61 | 26.712 |
| 19.34 | 4.662 | 55.91 | 31.750 |
| 23.15 | 5.447 | 60.90 | 33.583 |
| 31.46 | 7.920 | - | - |
| 33.53 | 9.471 | - | - |

Fig. 3 indicates that the viscosity of the ICl - $C_6H_5CONH_2$ system approaches an S-curve.

Several viscosity isotherms of this sort have been described in the literature[7]. In particular, they were obtained by M.I.Usanovich for the sulfuric acid - nitrobenzene system[8], the arsenic trichloride - ethyl ether system[8], and several others. Usanovich gave a theoretical explanation for such isotherms and called them S-curves[10].

Isotherms of this type often reflect chemical interaction between the system

components, resulting in the formation of coordination compounds.

An example of this is the $PCl_5$ - $Br_2$ system. Thermal analysis of this system, carried out by V.A.Plotnikov and S.I.Yakubson[11], indicated the presence of the coordination compound $PCl_5 \cdot 5Br_2$. They then isolated this compound from a hydrogen-sulfide solution. Recently, S.I.Yakubson has investigated the viscosity of the $PCl_5$ - $Br_2$ system at 25, 35, and 50°, finding that the isotherms were S-shaped[12].

S.I.Yakubson obtained the same sort of isotherm for the $CH_3CONH_2$ - $Br_2$ system[12]; electrochemical investigation proved that a coordination compound was formed in this system[13].

Lastly, it must be reiterated that thermal analysis of the $C_6H_5CONH_2$ - ICl system quite definitely indicated the formation of an equimolar coordination compound in this system.

## EVALUATION OF RESEARCH RESULTS

Measurement of the viscosity of the $CH_3CONH_2$ - ICl system proved beyond a doubt that the coordination compound $2CH_3CONH_2 \cdot ICl$ was present in it.

As the concentration of acetamide is increased, the viscosity of this system rises rather rapidly. It is quite possible that this circumstance, together with other factors, was responsible for the difficulties referred to above, encountered in our endeavors to investigate the $CH_3CONH_2$ - ICl system by the method of thermal analysis.

Instances of this sort, in which the viscosity isotherms exhibit a marked maximum, while the fusibility curves of the same system give no reason to expect the formation of new compounds, have been encountered more than once in the literature. N.S.Kurnakov explains these phenomena as follows: the conditions existing in a viscous liquid are unfavorable for the crystallization of the compound formed. In such cases, according to N.S.Kurnakov, viscosimetry is superior to thermal analysis as a method of physico-chemical analysis[3].

The existence of only one maximum, corresponding to a coordination compound $2CH_3CONH_2 \cdot ICl$, on the viscosity isotherm of the $CH_3CONH_2$ - ICl system and the absence of a maximum at the point corresponding to the equimolar compound $CH_3CONH_2 \cdot ICl$, discovered during the investigation of nitrobenzene solutions of this system[1], do not rule out the possibility of the simultaneous existence of the latter coordination compound.

As has been stated in the introduction to this paper, when there are several compounds in the liquid phase, as a rule, only those are exhibited on the viscosity isotherm which are less dissociated than the others. In this case, $2CH_3CONH_2 \cdot ICl$ is such a compound.

In the nitrobenzene solutions, the $2CH_3CONH_2 \cdot ICl \rightleftarrows CH_3CONH_2 \cdot ICl + CH_3CONH_2$ equilibrium is probably displaced toward the right.

If we assume that the coordination compound $CH_3CONH_2 \cdot ICl$, solvated with another molecule of acetamide, is really the most complicated of these coordination compounds, we may suppose that when this coordination compound $CH_3CONH_2 \cdot ICl$ is dissolved in nitrobenzene, it is solvated with a molecule of $C_6H_5NO_2$, which may result in the above-mentioned shift of the equilibrium to the right, and thus only the $CH_3CONH_2 \cdot ICl$ coordination compound is detected in the nitrobenzene solution.

A comparison of the viscosity isotherm and the fusibility diagram of the $C_6H_5CONH_2$ - ICl system indicates that that coordination compound $C_6H_5CONH_2 \cdot ICl$, detected by thermal analysis, is partially dissociated into its constituents in the liquid state, as a result of which the viscosity isotherm merely shows that a coordination compound is formed in this system without indicating the quantitative ratio

between the components of the coordination compound.

According to M.I.Usanovich[10], the S-curves of internal friction in binary systems are produced whenever one of the system components is an associated liquid, the compound that is formed being the normal liquid.

The first of these conditions applies to the given system, since iodine chloride is an associated liquid according to Cornog and Karges[14].

## SUMMARY

1. The viscosity of the ICl - $CH_3CONH_2$ system has been measured at 25, 35, and 45° for concentrations of $CH_3CONH_2$ ranging from 0 to 77.54 mol. %.

2. At all three temperatures, a maximum invariant with temperature is found, corresponding to the formation of the coordination compound $2CH_3CONH_2 \cdot ICl$.

3. The viscosity of the ICl - $C_6H_5CONH_2$ system has been measured at 50° for concentrations of $C_6H_5CONH_2$ ranging from 0 to 60.90 mol %. The viscosity isotherm is S-shaped.

4. The viscosity diagrams of these systems were compared with the results of the investigation of the system by other methods of physico-chemical analysis.

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# CLASSIFICATION OF DIAGRAMS IN THE VOLUMETRIC ANALYSIS OF LIQUID BINARY SYSTEMS

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We now possess classifications of the composition - property diagrams for most of the methods used in physico-chemical analysis (viscosity, refractometry, surface tension, heat of mixing, etc.)[1]. But, so far as we know, there is no such classification for the volumetric method of physico-chemical analysis.

Development of a classification for this method is of considerable importance, inasmuch as a large amount of data has been accumulated on the specific gravity of binary systems, both in specialized researches and in research on other system properties (viscosity, dielectric constant, etc.). Moreover, the volumetric investigation of systems is easily accomplished, requiring no complicating instrumentation and equaling other methods of physico-chemical analysis in precision of measurement.

The point of departure in working out a classification for any method of physico-chemical analysis is finding the shape of the diagram for an ideal system. In the present case, the search for this diagram shape involves no difficulties, inasmuch as ideal systems are usually defined as systems that are formed without shrinkage. The specific gravity of such a binary system is represented by a straight line when its composition is expressed in parts by volume, the shrinkage at any point equaling zero. We have previously established[2] that in this case the atomic concentration likewise varies linearly. Moreover, one of the present authors has shown that the degree of chemical interaction in the system may be judged by the differences between the experimental values of the atomic concentration and those computed for a mechanical mixture[2] (an ideal system). Henceforth, we shall denote this discrepancy by $\Delta A$. It follows from what has been said that $\Delta A$ is zero for an ideal system at any system composition.

In the present paper we intend to essay a classification of atomic concentration - composition diagrams on the basis of a large quantity of collected and worked-up data. Whenever one of the system components is a strong electrolyte by itself (fused salts, aqueous salt solutions, and strong acids or bases), these diagrams exhibit a number of singular features. In particular, expansion rather than shrinkage is sometimes observed in these cases during the formation of a chemical compound. This effect is specific only for the above-mentioned systems. In the present paper we shall confine outselves to a consideration of systems that do not include strong electrolytes.

As has been done for other properties[1], we consider it most convenient to subdivide the systems studied by the volumetric method into four basic groups.

1. Ideal systems. This group includes the systems consisting of liquids that do not interact chemically, with an unchanged degree of dissociation. Specific gravity and atomic concentration vary linearly when the system composition is expressed in parts by volume. $\Delta A$ and shrinkage are both zero (Fig. 1a).

2. Systems with an associated component, which breaks down into simpler

particles when dissolved. In these systems, the atomic concentration and specific gravity are represented by curves that are concave toward the composition axis, when the composition is expressed in per cent by volume. $\Delta A$ is negative for every composition. Mixing the components together causes expansion (Fig. 1b).

3. Systems in which the initial components form undissociated or slightly dissociated chemical compounds. Here the curves representing the atomic concentration or the specific gravity are convex upward when the system composition is expressed in per cent by volume. Mixing the components together is accompanied by shrinkage. $\Delta A$ runs along the composition of one of the chemical compounds (Fig. 1c).

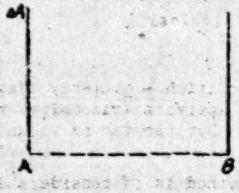


Fig. 1a.

Fig. 1b.

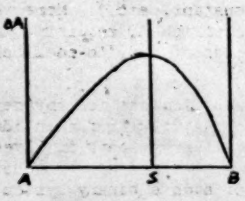


Fig. 1c.

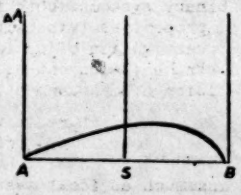


Fig. 1d.

4. Systems in which the formation of a chemical compound is paralleled by the dissociation of one or both associated components. As a rule, the curves of atomic concentration and specific gravity are convex upward. Hence, the systems usually exhibit a slight shrinkage. The absolute value of $\Delta A$ is small. The maximum $\Delta A$ may not correspond to the composition of the chemical compound formed (Fig. 1d).

Let us now turn to a more detailed consideration of these four types of diagrams.

## 1. Ideal Systems

Notwithstanding numerous endeavors to do so, the shape of the ideal curve has not yet been established for a number of composition - property diagrams (viscosity, refractive index, etc.)[1]. For volumetric functions, however, the shape of this diagram is set by the very definition of an ideal system, as has been set forth above. The expected linearity of specific gravities and atomic concentrations when the composition is expressed in per cent by volume may be shown for a great many systems. Examples of this sort of system ("isofluid," in Biron's terminology[4]) are: $C_2H_5I$ - $CH_3COOC_2H_5$; $C_6H_6$ - $CCl_4$; $C_6H_6$ - $C_6H_5Br$; $CH_3COOCH_3$ - $HCOOC_2H_5$; $C_7H_{16}$ - $C_6H_5Cl$; $C_7H_{16}$ - $C_6H_5CH_3$; $CCl_4$ - $C_2H_4Br_2$; $C_6H_6$ - $C_2H_4Br_2$; etc.

It is worthy of note that the viscosity isotherms for these systems have

various shapes. In the $C_2H_5I$ - $CH_3COOC_2H_5$ system, for instance, the viscosity isotherm has a minimum; in the $C_6H_6$ - $CCl_4$ system this curve is convex toward the composition axis; and it is a straight line in the $C_6H_6$ - $C_6H_5Br$ system.

Mixtures of two associated liquids of closely related chemical nature likewise yield diagrams of this type. The $CH_3OH$ - $C_3H_7OH$ and HCOOH - $CH_3COOH$ systems are examples of this type.

It should be mentioned in this connection that the diagrams of molecular weight versus composition for two alcohols are likewise linear, as has been shown by V.V.Udovenko[5].

V.Y.Anosov[1] has asserted that there are no rigorously ideal systems and that nearly all substances exhibit a tendency toward association or chemical interaction. Apparently, this assertion is fundamentally correct. In a number of systems formed from nonreacting and, apparently, unassociated components, we find a regular, even though extremely minute, departure of the atomic concentrations from linearity.

The following systems are examples of systems with slight, but regularly negative, values of $\Delta A$[6]:

$CCl_4$ - $CS_2$; $C_6H_5CH_3$ - $CS_2$; $CHCl_3$ - $CS_2$; $C_2H_4Br_2$ - $CS_2$; $C_7H_{16}$ - $CS_2$; $CCl_4$ - $CHCl_3$; $C_5H_{12}$ - $(C_2H_5)_2O$; $C_7H_{16}$ - $C_2H_4Br_2$; etc.

Systems with slight, but regularly positive, values of $\Delta A$ include: $C_7H_{16}$ - L - $C_{10}H_7Br$; $C_2H_4Br_2$ - $CHCl_3$; $CS_2$ - $C_6H_5Br$, etc.

2. Systems with an Associated Component, Which Breaks Down When Dissolved.

The formation of chemical compounds in these systems (nonelectrolytes) is always accompanied by contraction, i.e., by an increase in the atomic concentration as compared to the mean computed values. It is therefore quite natural to expect the reverse to happen when the associated molecules are dissociated -- expansion, or a diminution of the atomic concentration as compared with the values computed for mechanical mixtures.

In fact, in systems with an associated component (an organic acid, an alcohol, a ketone, and the like), which dissociates into a "normal" liquid when dissolved, the values of atomic concentration and specific gravity are always smaller than those computed for ideal systems. Here $\Delta A$ is always less than zero, i.e., expansion is manifested at all points.

Examples of this are the following systems: $C_6H_6$ - $CH_3COOH$; $CCl_4$ - $CH_3COCH_3$; $CS_2$ - $CH_3COCH_3$; $C_2H_5Br$ - $CH_3COOH$; $C_7H_8$ - $CH_3COOH$; $CCl_4$ - $C_3H_7OH$; $CH_3I$ - $CH_3COCH_3$; $CS_2$ - $C_3H_7OH$; etc.

In some of these systems the viscosity isotherms have a minimum or are markedly concave toward the composition axis.

It is our opinion that the use of volumetric methods to determine the existence of dissociation of associated components in a system yields more reliable results than the viscosity method, inasmuch as minima and convexities toward the composition axis may be found on viscosity isotherms even in ideal systems, as indicated above.

3. Systems in Which Chemical Compounds are Formed

The formation of chemical compounds is accompanied by considerable shrinkage, as a result of which the atomic concentration and the specific gravity exceed the values computed from the additivity rule for any component ratio. Accordingly, $\Delta A$ is positive at all points. It is characteristic that in this instance the maximum value of $\Delta A$ corresponds to the composition of the compound formed as a result of the reaction, not only in singular systems, but in many other systems with partially

dissociated compounds, as had already been noted by us at an earlier date. In this instance the singular diagrams are fundamentally different from other types in that here the extreme values of all differential volumetric functions correspond to the compound's composition.

Anosov[1] has shown that in a singular system the composition - property curve consists of two intersecting branches of a hyperbola. Accordingly, in our particular case of atomic - concentration study, we arrive at the conclusion that in singular systems the atomic concentration - composition curves and hence the $\Delta A$ - composition curves have the following shape.

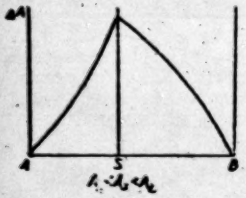

Fig. 2.

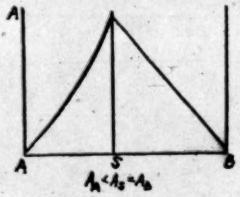

Fig. 3.

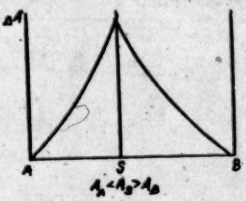

Fig. 4

I. Where A and $\Delta A$ vary complementarily in the diagram, the curves are convex toward the composition axis.

II. Where the changes of A and $\Delta A$ are antithetical in the diagram, the curves are convex upward, away from the composition axis.

III. Where the values of A and $\Delta A$ are constant, the corresponding sections of the curves are rectilinear.

We can predict three types of $\Delta A$ - composition diagrams corresponding to the cases discussed above, illustrated schematically in Figs. 2, 3) and 4.

Diagrams of the first type (Fig. 2) have been plotted for the $SnCl_4$ - $RCOOC_2H_5$ system.

A diagram closely resembling the type shown in Fig. 3 has been plotted for the $CNSC_2H_5$ - $C_5H_{10}NH$ system. No diagrams corresponding to the type shown in Fig. 4 have been found as yet. $\Delta A$-composition diagrams like the one illustrated schematically in Fig. 5 have been plotted for many systems in which chemical compounds are formed. In these diagrams the maximum value of $\Delta A$ corresponds to the composition of one of the compounds formed in the system. According to our interpretation, diagrams of this sort indicate that several compounds are present in the system.

One of them is detected by the location of the $\Delta A$ maximum. The region in which

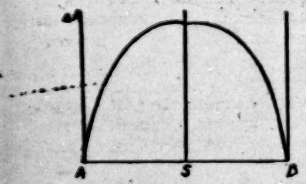

Fig. 5.

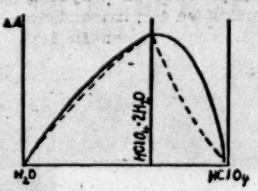

Fig. 6.

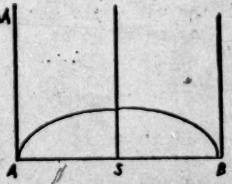

Fig. 7.

the other compounds lie may be found by using the rules set up for singular systems outlined above.

By way of example, let us consider the $HClO_4$ - $H_2O$ system. The $\Delta A$ - composition diagram for this system is given in Fig. 6. The $\Delta A$ maximum corresponds to the composition $HClO_4 \cdot 2H_2O$.

If $HClO_4 \cdot 2H_2O$ were the sole compound existent in the system, the diagram would exhibit the shape shown by the dotted curve.

The appreciable deviation from the computed values, particularly in the right-hand portion of the diagram, can be due solely to the presence of other compounds.

Actually, in the solid state we know of the existence of the extremely stable monohydrate $HClO_4 \cdot H_2O$, in addition to the foregoing dihydrate, besides a number of other hydrates.

The following are examples of systems in which several chemical compounds are formed: $HNO_3$ - $H_2O$; HF - $H_2O$; $H_2SO_4$ - $H_2O$; $H_3PO_4$ - $H_2O$; $N_2H_4$ - $H_2O$; $H_2SO_4$ — — $(C_2H_5)_2O$; etc.

## 4. "Irrational" Systems

When the formation of a chemical compound in the system is accompanied by the dissociation of one of the associated components, the general shape of the $\Delta A$ — composition diagram is somewhat more complicated.

Superposition of these directly opposed processes first affects the absolute value of $\Delta A$; in the foregoing systems $\Delta A$ is negligibly small, as a rule. As for the shape of the $\Delta A$ — composition diagrams, they are rather diversified in this group of systems, generally falling into the following three types, however:

a) Diagrams with a depressed, washed out maximum, exhibited by the following systems: $C_6H_5OH$ - $C_6H_5NH_2$; $CH_3COCH_3$ - HCOOH; $C_6H_4(NO_2)_2$ - $C_6H_4COOH$ (Fig. 7).

b) Diagrams with a maximum that does not correspond to the compound's composition, nor to any other rational ratio; the following are examples of this type of system: $CH_3COOH$ - $H_2O$; $CH_3OH$ - $H_2O$; $CH_3COCH_3$ - - $CH_3COOH$; $C_6H_5OH$ - $CH_3COCH_3$ (Fig. 8).

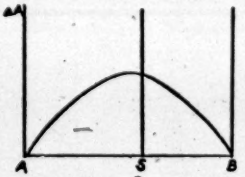

Fig. 8

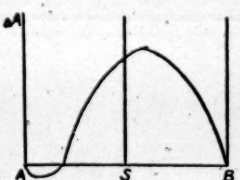

Fig. 9

c) Diagrams with S-shaped curves. In some regions of the diagram the breakdown of the associated component ($\Delta A < 0$) plays the decisive role, whereas in other regions the formation of a chemical compound ($\Delta A < 0$) is decisive. Generally speaking, the $\Delta A$ maximum does not lie at any rational ratio. Diagrams of this type are found in systems of the following type: $SbCl_3$ - $C_6H_6$; $SbCl_3$ - $CH(C_6H_5)_3$; and $SbCl_3$ - $C_{10}H_8$ (Fig. 9).


## SUMMARY

A classification is proposed for diagrams of specific gravity and atomic concentration for the magnitude of the deviation of atomic concentration from the additivity rule ($\Delta A$), and for the volumetric changes (shrinkage) that take place during the volumetric analysis of two-component liquid systems.


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*Evidently typographical error, since JAC 1948 would be Vol. 21.

# PHYSICO-CHEMICAL INVESTIGATION OF THE SILVER NITRATE - SILVER IODIDE SYSTEM IN THE MOLTEN STATE

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Academician N.S.Kurnakov[1] distinguishes two major types of diagrams of homogeneous systems -- diagrams with nonsingular elements, having no peculiar or singular points, and diagrams with singular elements. Diagrams with nonsingular elements are quite common. In the ideal state, the property curves in such diagrams are straight (additive) lines. They indicate the absence of chemical interaction between the system's components. Departures from this rule are common. These deviations may lie above the additive straight line (positive) or below it (negative).

They may be related to the appearance of new kinds of molecules within the system; the chemical transformations involved may result in complicating the molecular composition of the components or, conversely, may simplify it.

Corresponding to different stages of transformation, the positive curves gradually change into curves with a maximum, and the negative curves into curves with a minimum. The locations of these maxima and minima undergo continuous displacement in the diagram. Their composition does not remain constant nor does it obey the law of multiple proportions. These shifts set in as a result of a change in the equilibrium factors.

The other major type of diagram of homogeneous systems comprises diagrams with singular points located at the intersections of the two branches. The presence of such points is due to the existence in the liquid medium of compounds formed from the system's components.

At the present time the singularity problem has been solved for organic systems. This problem has also been solved for metals in the solid state and for salt systems in solution.

The systematic investigation of salt systems in the molten state to establish the correspondence between the structural diagram and the diagram of physico-chemical properties was first undertaken in 1932 by A.G. Bergman[2], first in the State Institute of Applied Chemistry, and then in the USSR Academy of Sciences, where our own research was initiated. In a previous paper[3] we demonstrated that the doctrine of singularity of elements is confirmed for salts in the molten state as well. The singular elements discovered by us on the isotherms of specific conductance and viscosity lie on the ordinates of definite compounds. We found a sharply expressed minimum on the isotherms of specific conductance of the silver nitrate – thallium nitrate system; the lower the corresponding melting point, the sharper this minimum was. As the temperature is increased, the minimum becomes more washed-out and is shifted

toward the component with the lower value for the property in question.

The viscosity isotherms exhibited a marked maximum; the lower the melting point, the sharper this maximum was. The higher the temperature, the flatter this maximum becomes and the more it shifts toward the thallium nitrate side of the diagram.

We were interested in tracing the changes in specific conductance, viscosity, and specific gravity in the silver nitrate - silver iodide system. The system chosen for our research has a relatively low melting point and is characterized by the presence of compounds within it. According to Scarpe, one compound has been proved to exist in this system, with a component ratio of 3:2.

Investigating the fusibility of this system, N.S.Dombrovskaya[4] found that two compounds were present. In our research, the initial substances were recrystallized and then fused. The operational methods used in investigating specific conductance, viscosity, and specific gravity have been described in the paper already cited[3].

Fifteen different compositions were used in our research on the specific conductance of the silver nitrate - silver iodide system; 14 compositions were used in our viscosity investigation; and 14 compositions were used in exploring the specific gravity.

The lower limit was fixed by the appearance of the solid phase, and the upper limits were as follows: the beginning of decomposition of the nitrates, i.e., 300°, for the specific conductance; and 225° for the viscosity and specific gravity.

These polytherms were used to plot isotherms 25° apart.

The numerical data on the specific conductance of the system are given in Table 1; the numerical data on the viscosity and specific gravity are listed in Tables 2 and 3, respectively.

TABLE 1

Specific Conductance of the Silver Nitrate - Silver Iodide System

| Composition % by weight | | Specific conductance at | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $AgNO_3$ | AgI | 300° | 275° | 250° | 225° | 200° | 175° | 150° | 125° |
| 100 | - | 0.993 | 0.907 | 0.804 | 0.691 | - | - | - | - |
| 90 | 10 | 0.980 | 0.882 | 0.784 | 0.669 | 0.570 | - | - | - |
| 80 | 20 | 0.993 | 0.900 | 0.800 | 0.705 | 0.598 | 0.500 | 0.388 | - |
| 75 | 25 | 1.01 | 0.923 | 0.831 | 0.735 | 0.630 | 0.528 | 0.418 | 0.315 |
| 73 | 27 | 1.00 | 0.915 | 0.824 | 0.726 | 0.620 | 0.522 | 0.416 | 0.320 |
| 70 | 30 | 1.02 | 0.927 | 0.831 | 0.738 | 0.630 | 0.528 | 0.426 | 0.322 |
| 67 | 33 | 1.03 | 0.943 | 0.856 | 0.765 | 0 656 | 0.554 | 0.451 | 0.348 |
| 65 | 35 | 1.04 | 0.955 | 0.867 | 0.778 | 0.672 | 0.570 | 0.470 | 0.368 |
| 63 | 37 | 1.05 | 0.976 | 0.885 | 0.791 | 0.683 | 0.584 | 0.478 | 0.382 |
| 60 | 40 | 1.07 | 0.994 | 0.907 | 0.807 | 0.700 | 0.608 | 0.509 | 0.400 |
| 57 | 43 | 1.10 | 1.02 | 0.935 | 0.835 | 0.735 | 0.635 | 0.524 | 0.424 |
| 54 | 46 | 1.13 | 1.04 | 0.963 | 0.874 | 0.765 | 0.654 | 0.561 | 0.458 |
| 52 | 48 | 1.12 | 1.03 | 0.959 | 0.870 | 0.756 | 0.659 | 0.558 | 0.461 |
| 50 | 50 | 1.15 | 1.07 | 0.995 | 0.904 | 0.794 | 0.711 | 0.598 | 0.491 |
| 47 | 53 | 1.19 | 1.09 | 1.01 | 0.923 | 0.835 | 0.726 | 0.628 | 0.501. |

The specific conductance isotherms are shown in Fig. 1.

As in the silver nitrate - thallium nitrate system, the specific conductance curves for the silver nitrate - silver iodide system as a function of temperature

in the molten state are nearly straight lines, except in the regions close to the melting points of these mixtures.

The specific conductance isotherms do not obey the additivity law, but are generally concave upward.

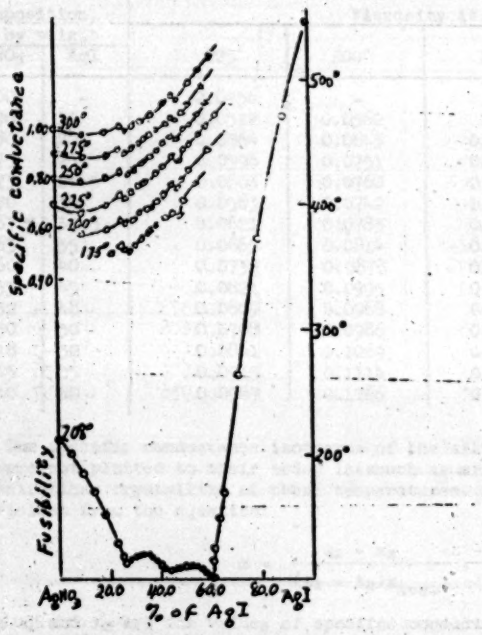


Fig. 1. Fusibility diagram and isotherms of specific conductance of the binary system silver nitrate - silver iodide in the molten state.

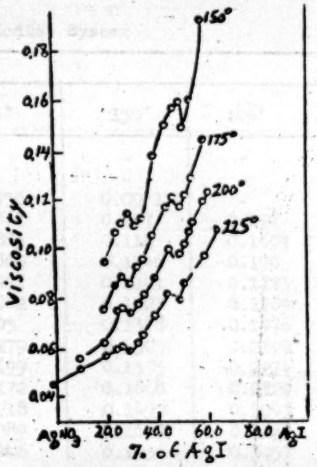


Figure 2. Viscosity isotherms of the binary system silver nitrate - silver iodide in the molten state.

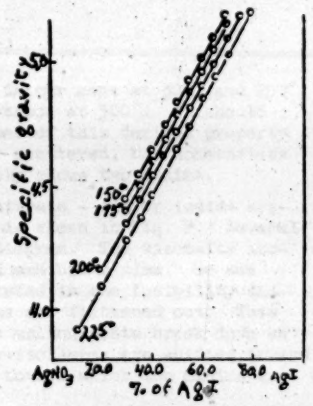


Fig. 3. Specific gravity isotherms of the binary system silver nitrate - silver iodide in the molten state.

It is worthy of note that melts containing less of the second component, i.e., silver iodide, exhibit a sharp break in the specific conductance at the instant of solidification. The isotherms of specific conductance for the silver nitrate - silver iodide system exhibit two fairly sharp minima. These minima correspond to compounds already detected in the fusibility curve. The shift of these minima toward the silver nitrate side of the diagram,

that is, the less conducting component, is likewise noticeable. As the temperature is increased, these two fairly sharp minima gradually smooth out, indicating dissociation of the compound formed in the melt.

TABLE 2

Viscosity of the Silver Nitrate - Silver Iodide System

| Composition, % by weight | | Viscosity at: | | | | |
|---|---|---|---|---|---|---|
| $AgNO_3$ | AgI | 225° | 200° | 175° | 150° | 125° |
| 100 | - | 0.0456 | - | - | - | - |
| 90 | 10 | 0.0512 | 0.0562 | - | - | - |
| 80 | 20 | 0.0564 | 0.0643 | 0.0755 | 0.0941 | - |
| 75 | 25 | 0.0596 | 0.0751 | 0.0861 | 0.107 | 0.157 |
| 73.5 | 26.5 | 0.0603 | 0.0760 | 0.0885 | 0.110 | 0.1609 |
| 70 | 30 | 0.0583 | 0.0742 | 0.0863 | 0.1146 | 0.170 |
| 67.5 | 32.5 | 0.0621 | 0.0785 | 0.0927 | 0.1101 | 0.1773 |
| 65 | 35 | 0.0665 | 0.0814 | 0.0942 | 0.1123 | 0.1709 |
| 60 | 40 | 0.0732 | 0.0878 | 0.105 | 0.1378 | 0.1976 |
| 55 | 45 | 0.0821 | 0.0995 | 0.1179 | 0.1505 | 0.2192 |
| 52 | 48 | 0.0809 | 0.0968 | 0.1199 | 0.1573 | 0.2274 |
| 50 | 50 | 0.0798 | 0.0986 | 0.1172 | 0.1608 | 0.2320 |
| 48 | 52 | 0.0861 | 0.1069 | 0.1218 | 0.1499 | 0.2943 |
| 45 | 55 | 0.0915 | 0.1114 | 0.1289 | 0.1609 | 0.2256 |
| 40 | 60 | 0.0967 | 0.1186 | 0.1446 | 0.1936 | 0.3057 |

The specific conductance isotherms of the silver nitrate - silver iodide system were not plotted to their ends, inasmuch as mixtures with high silver iodide concentrations crystallize at these temperatures. We calculated the temperature coefficient from the equation:

$$\alpha = \frac{x_1 - x_2}{(t_1 - t_2)x_{ave.}},$$

where $x_1$ and $x_2$ are the values of specific conductance in our case at 300° and 250°, $t_1 - t_2 = 50°$, and $x_{ave.}$ is the average specific conductance at 300°. It should be noted that there is a considerable error in the values of this derived property at relatively high temperatures. The points are rather scattered, but nonetheless the composition - temperature coefficient diagram clearly shows two maxima.

The composition - property diagram of the silver nitrate - silver iodide system on which the viscosity isotherms have been plotted is shown in Fig. 2. Several characteristic features attract our attention in this diagram. The viscosity isotherms of the silver nitrate - silver iodide system all exhibit maxima. We see two such maxima; they correspond to the compounds indicated in the fusibility diagram. The higher the temperature, the more these maxima are flattened out. This indicates that the coordination compounds formed in the molten state break down as the temperature is raised. The maxima on the viscosity isotherms are shifted toward the silver nitrate side of the diagram, i.e., the side toward which the minima are shifted in the isotherms of specific conductance.

The isotherms of specific gravity are shown in Fig. 3. They exhibited no singular points at the ordinates of compounds. The specific gravity isotherms follow the additivity law almost exactly, with a negligible deviation toward the

composition axis.

TABLE 3

Specific Gravity of the Silver Nitrate - Silver Iodide System

| Composition % by weight | | Specific gravity at: | | | |
|---|---|---|---|---|---|
| $AgNO_3$ | AgI | 225° | 200° | 175° | 150° |
| 100 | - | 4.092 | - | - | - |
| 90 | 10 | 4.108 | 4.164 | - | - |
| 80 | 20 | 4.285 | 4.346 | 4.398 | 4.418 |
| 75 | 25 | 4.368 | 4.442 | 4.497 | 4.513 |
| 70 | 30 | 4.466 | 4.538 | 4.605 | 4.638 |
| 65 | 35 | 4.563 | 4.629 | 4.698 | 4.727 |
| 60 | 40 | 4.652 | 4.720 | 4.782 | 4.816 |
| 55 | 45 | 4.742 | 4.815 | 4.873 | 4.911 |
| 50 | 50 | 4.835 | 4.904 | 4.965 | 5.013 |
| 45 | 55 | 4.929 | 4.993 | 5.054 | 5.102 |
| 40 | 60 | 5.024 | 5.000 | 5.141 | 5.193 |


SUMMARY

1. The specific conductance, viscosity, and specific gravity of the silver nitrate - silver iodide system have been investigated in the molten state of the system.

2. Elements of singularity have been noted on the isotherms of specific conductance and viscosity in the silver nitrate - silver iodide system in the molten state, indicating a certain analogy between the behavior of molten salts and that of liquid organic systems, metals in the solid state, and salt systems in solution.

3. Two minima are observed on the isotherms of specific conductance, corresponding to the ordinates of definite compounds discovered in the fusibility diagram. As the temperature is raised, these minima flatten out and are shifted toward the silver nitrate, indicating growing dissociation of the compound in the melt as the temperature rises.

4. The viscosity isotherms of the silver nitrate - silver iodide system exhibit two maxima, which also correspond to the ordinates of definite compounds in the fusibility diagram. As the temperature is increased, these maxima flatten out and shift toward the silver nitrate side of the diagram.

5. The isotherms of specific gravity exhibited no singular elements and reflected no chemical action within the system.


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* Cf CB translation p. 789 ff.

# POLAROGRAPHIC INVESTIGATION OF COORDINATION COMPOUNDS OF COPPER AND PYRIDINE

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The ions of univalent and bivalent copper form numerous coordination compounds with neutral molecules and ions of other substances. The composition and stability of several coordination compounds of copper have been established or confirmed by means of polarographic measurements. Stackelberg and Freyhold [1], for example, succeeded in showing that bivalent copper forms several coordination coordination compounds in an aqueous solution of ammonia, their composition depending upon the amount of ammonia in solution. They confirmed the existence of the ions $[Cu(NH_3)_2]^{++}$, $[Cu(NH_3)_4]^{++}$, etc. For univalent copper they discovered a complex ion $[Cu(NH_3)_2]^{+}$. For all these complex ions the authors found the computed values of the instability constant. The same authors investigated the reduction of copper from solutions containing chlorine ions in various concentrations. Here, too, complex ions of copper and chlorine are formed, containing varying percentages of the latter element. As the chlorine ion concentration in the solution changes, the percentage of coordination compounds of one composition or another also changes.

During an investigation of the reduction of copper at a mercury drop electrode from solutions containing α-aminoacetic acid and α-aminopropionic acid in various concentrations [2], it was shown that bivalent copper can form coordination compounds of the following composition:

$[Cu(NH_2CH_2COO)_2]$, $[Cu(CH_3NH_2CHCOO)_2]$, and $[Cu(NH_2CH_2COO)_3]^-$.

The reduction of bivalent copper from solutions of its coordination compounds in triethanolamine has also been explored [3].

The cited data thus indicate that the polarographic method of analysis may be employed to determine the formulas of complex ions or molecules of varying composition in equilibrium with one another and with the substance constituting outer sphere of the coordination compound.

The first objects of our research were the coordination compounds of copper and pyridine, whose composition and stability have not yet been measured polarographically.

In the formation of coordination compounds the half-wave reduction potential is shifted toward negative values, inasmuch as the ion concentration of the metal that governs the numerical value of the potential of the mercury drop electrode is diminished.

The potential shift depends on the instability constant of the coordination compound ($k_c$), the coordination number (p), the valence of the ions of the coordination component to be reduced, and the concentration of the substance constituting the outer sphere of the coordination compound $C_x$, according to the equation:

$$(\pi_{1/2})_c - (\pi_{1/2})_h = \frac{RT}{nF} \ln k_c - p \frac{RT}{nF} \ln C_x ,$$

where $(\pi_{1/2})_c$ and $(\pi_{1/2})_h$ are the half-wave potentials for formation of the coordination compound and for reduction of the hydrated ions, i.e., when no coordination compound is formed. Use of the foregoing equation presupposes that the diffusion coefficients of the coordination compounds and of the simple hydrated ions are identical, and that dissociation of the coordination compound is not a factor limiting the diffusion of the reducible ions to the surface of the electrode or the electrode process.

Differentiating Equation (1), we get:

$$\frac{d(\pi_{1/2})}{d \lg C_x} = - p \frac{RT}{nF} , \qquad (1)$$

which takes on this form for room temperature:

$$\frac{d(\pi_{1/2})}{d \lg C_x} = - p \frac{0.059}{n} . \qquad (2)$$

## EXPERIMENTAL

Solutions of copper nitrate, with a concentration of the order of $10^{-3}$N, were prepared for this research. We used a 0.01N solution of potassium nitrate as the indifferent electrolyte. During polarography the pyridine concentration was varied from 0.005 mol per liter to 2.0 mols per liter. The copper maxima were suppressed by adding gelatin to the solution. The polarographs were recorded with all air excluded. To effect this, a stream of electrolytic hydrogen was blown through the solution of copper and potassium nitrates in the electrolyzer for 30 minutes, after which the requisite quantity of pyridine was added, and a current of hydrogen was again passed through the solution. We thus avoided changing the pyridine concentration while expelling the oxygen. To maintain the temperature of the electrolyzer constant, the latter was immersed in a thermostat at a temperature of 25 $\pm$ 0.5°. A saturated calomel electrode was used as a comparison electrode, its potential being assumed to be zero.

The polarogram was recorded with a visual polarograph in the range of +0.5 to 1.0 volt. The mercury drop electrode had the following characteristic:

$$m^{2/3} t^{1/6} = 1.35 \text{ mg}^{2/3} \text{ sec}^{-1/2}.$$

When copper is reduced from a neutral solution containing potassium nitrate and a slight amount of gelatin, the polarogram exhibits a single diffusion wave, corresponding to the conversion of bivalent copper into a dilute amalgam:

$$Cu^{++} + 2e + Hg \rightleftarrows Cu(Hg).$$

The half-wave potential corresponding to this process is 0.02 volt with respect to the saturated calomel electrode.

The introduction of small amounts of pyridine does not appreciably change the form of the diffusion wave for the reduction of bivalent copper. Only when the pyridine in the solution attains 0.015-0.02 mol per liter is the wave divided in two, as it were, and as the concentration of pyridine is raised still higher, the polarogram plotted for the copper solution exhibits two clearly distinct waves with different half-wave potentials (Fig. 1). Apparently, the presence of pyridine in the solution facilitates the stabilization of the univalent ion formed during the reduction of the ion of bivalent copper, the former ion forming fairly stable

coordination compounds with the pyridine molecules in solution.

Determining the numerical value of the potentials of the separate waves we noticed that for the first diffusion wave, corresponding to the conversion of bivalent copper into univalent copper, the half-wave potential remains constant and

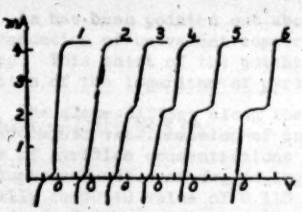


Fig. 1. Polarogram of copper waves in a concentration of 0.0012 mol per liter against a background of 0.01N $KNO_3$ in the presence of pyridine.

1-Without pyridine; 2-In the presence of 0.0076 mol /liter of pyridine; 3-0.064 mol/liter; 4-0.285 mol/liter; 5-0.812 mol/liter; 6-1.11 mol /liter; the abscissa graduations are 0.2 volt each.

TABLE 1

Half-Wave Potential of Copper ($1.2 \cdot 10^{-3}$ Mol/Liter) in the Presence of Potassium Nitrate (0.01N) and Pyridine. Temperature 25°.

| Pyridine concentration, mols/liter | Half-wave potential, volts | |
|---|---|---|
| 0.015 | +0.04 | -0.10 |
| 0.023 | 0.04 | 0.11 |
| 0.031 | - | 0.13 |
| 0.042 | - | 0.14 |
| 0.064 | - | 0.17 |
| 0.11 | - | 0.20 |
| 0.13 | +0.04 | 0.20 |
| 0.193 | - | 0.21 |
| 0.285 | - | 0.24 |
| 0.357 | - | 0.26 |
| 0.412 | - | 0.29 |
| 1.0 | -0.04 | 0.33 |
| 1.11 | - | 0.37 |
| 1.50 | - | 0.42 |
| 2.00 | -0.20 | 0.47 |

is independent of the pyridine concentration until the content of the latter in the polarographed solution reaches 1.0 - 1.1 mols per liter; only when this concentration is increased still more is the half-wave potential shifted toward negative values.

In contrast hereto, the half-wave potential of the second stage of copper reduction continuously shifts toward negative values as the pyridine concentration increases.

Fig. 2 graphically illustrates the variation of the potential of the individual waves with pyridine concentration in semilogarithmic coordinates.

The numerical values of the potentials ($\pi_{1/2}$) of copper reduction in the presence of various concentrations of pyridine are given in Table 1.

## EVALUATION OF RESULTS

Fig. 2 indicates that when the amount of pyridine in the solution is below 1.0 mol/liter, the ion of bivalent copper does not form coordination compounds with the former. As the percentage of pyridine in the solution continues to rise, a complex ion is formed, and as a result the half-wave potential shifts

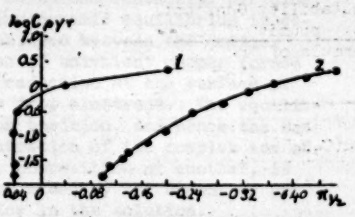


Fig. 2. Potential of copper reduction as a function of the logarithm of pyridine concentration.

1-First wave, 2-Second wave

sharply toward negative values.

Calculations using Equation(2) indicate that the complex ion $[Cu(C_5H_5N)_6]^{++}$ is formed. Apparently no other complex ions are present in detectable quantities in the solution, and if one of them were to be formed, the region of pyridine concentrations in which they could exist is extremely narrow.

As has been pointed out above, the second diffusion wave corresponding to the reduction of univalent copper to the metal, is shifted to more negative values. This shift of the potential of copper reduction, however, is not a linear function of the logarithm of pyridine concentration.

The slope differs along the different sections of Curve 2 (Fig. 2), corresponding to the formation of complex ions of different composition. In the range of pyridine concentrations extending from 0.025 mol/liter to 0.25 mol/liter, the numerical value of $d\pi_{1/2}/d \log C_X$ is 0.119 volt, which agrees with the theoretically computed value of 0.118 volt for the coordination number 2 of the complex ion. Thus, in this pyridine concentration range the complex ion $[Cu(C_5H_5N)_2]^+$ is formed and predominates.

Above the pyridine concentration of 0.25 mol/liter, say up to 0.8 mol/liter, the observed slope equals 0.185 volt, which corresponds to a coordination number of 3, for which the computed value of $d\pi_{1/2}/d \log C_X$ ought to be 0.177 volt. At these pyridine concentrations, therefore, the formula of the complex ion is $[Cu(C_5H_5N)_3]^+$.

A further rise in the pyridine concentration to 1.1 mol liter changes the slope, making it 0.238 volt instead of 0.236 volt for the coordination number of 4. In this pyridine concentration range the solution contains the complex ion $[Cu(C_5H_5N)_4]^+$.

At pyridine concentrations in excess of 1.1 - 1.2 mols/liter the observed value of $d\pi_{1/2}/d \log C_X$ is 0.4, which is quite close to the theoretical value of 0.36 volt for the coordination number of 6. Apparently, at this concentration the principal complex ion in the solution is $[Cu(C_5H_5N)_6]^+$. It should be noted that in the last case the discrepancy between the theoretical value of $d\pi_{1/2}/d \log C_X$ and the observed value is greatest. This may be due to errors in determining the half-wave potential. At high pyridine concentrations the shape of the diffusion wave changes noticeably, its upper section becoming markedly rounded and flattened. Moreover, at high pyridine concentrations the solution becomes cloudy, probably owing to the precipitation of salt, and the copper diffusion current is diminished somewhat.

TABLE 2

Instability Constants of Coordination Compounds of Copper and Pyridine

| Formula of the complex cation | Coordination number (P) | Instability constant |
|---|---|---|
| $[Cu(C_5H_5N)_2]^+$..... | 2 | $0.46 \cdot 10^{-3}$ |
| $[Cu(C_5H_5N)_3]^+$..... | 3 | $0.31 \cdot 10^{-4}$ |
| $[Cu(C_5H_5N)_4]^+$..... | 4 | $0.36 \cdot 10^{-5}$ |
| $[Cu(C_5H_5N)_6]^+$..... | 6 | $0.13 \cdot 10^{-6}$ |
| $[Cu(C_5H_5N)_6]^{++}$..... | 6 | 0.1 |

Our results indicate that in solutions containing pyridine, thermodynamic equilibrium is established between the complex ions of univalent copper formed by reduction at the surface of the drop electrode. The equilibrium position, and hence the concentration of the complex ion of one composition or another, is determined by the amount of pyridine in the solution.

At low pyridine concentrations, a complex ion with a coordination number of 2 predominates in the solution; as the pyridine concentration rises, the concentration of the complex ion with a coordination number of 3 increases, while the concentration of the complex ion .

with the coordination number of 2 drops, and so forth. We employed Equation (1) to calculate the instability constant of the coordination compounds. Our results are given in Table 2.

As is seen in Table 2, the stability of the coordination compounds formed rises with the coordination number. It may be stated at this point that for identical coordination numbers the stability of complex ions of univalent copper is much higher than that of complex ions of bivalent copper. This is probably why we were unable to detect complex cations of bivalent copper and pyridine with a coordination number lower than six in the solution.

We might also mention that Bjerrum's researches [4] on cuprammonium complex ions enabled him to establish that the stability of cuprammonium rose as the coordination number increased, both for univalent and for bivalent copper.

## SUMMARY

1. The reduction of copper from solutions containing varying percentages of pyridine has been investigated.

2. It has been established that in solutions containing pyridine the latter reacts with the copper ions, resulting in the formation of complex cations of various compositions.

3. The coordination numbers and the instability constants of the complex ions formed have been determined.

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# SYNTHESIS AND CONVERSIONS OF TERTIARY ALIPHATIC-AROMATIC ALCOHOLS OF THE ETHYLENE SERIES

## II. ACTION OF SULFURIC ACID ON METHYLPHENYLVINYLCARBINOL AND METHYLBENZYLVINYLCARBINOL

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In one of our previous papers [1] we established that the action of sulfuric acid on dimethylvinylcarbinol yields several products, formed by the hydration, dehydration, isomerization, and polymerization of the dimethylvinylcarbinol. The results of the researches of M.Z.Zalmanovich [2] and K.A.Oglobin [3] on the reaction of sulfuric acid with methylethylvinylcarbinol and dimethylisopropenylcarbinol agreed with our results. All of these researches dealt with aliphatic ethylenic alcohols, however, so that we felt it worth while to examine the action of sulfuric acid upon aliphatic-aromatic ethylenic alcohols. With this in view we synthesized methylphenylvinylcarbinol and methylbenzylvinylcarbinol [4] and explored their reactions with sulfuric acid. We succeeded in establishing the fact that 25% sulfuric acid cleaves methylphenylvinylcarbinol at room temperature, forming acetophenone, traces of benzaldehyde, and a polymer, when the quantity of aqueous solution of sulfuric acid used is ten times that of the methylphenylvinylcarbinol.

Ketone decomposition of unsaturated aldehydes and ketones by acids and bases has been known for a long time. Claisen [5] was the first to note that mesityl oxide breaks down into two molecules of acetone when reacted with extremely dilute sulfuric acid. Then Kondakov [6] found that when unsaturated aldehydes or ketones are distilled together with weak sulfuric or hydrochloric acid, they are cleaved into aldehydes or ketones with a lower number of carbon atoms than in the initial molecule. When cinnamic aldehyde is reacted with an alkali and lime, we get benzaldehyde and acetaldehyde [7]. V.V.Chelintsev [8] has shown that the action of sulfuric acid or of an alkali on unsaturated aldehydes and ketones causes some of the aldehydes to be replaced by others. V.V.Chelintsev believes that the cleavage process is possible only when the $>C=CH-CO-$ group is present.

In our instance, no such group was present when dilute sulfuric acid was reacted with methylphenylvinylcarbinol, and yet ketone decomposition of the unsaturated alcohol took place, resulting in the formation of a molecule of acetophenone from the molecule of methylphenylvinylcarbinol.

We have been unable, as yet, to isolate and identify the product obtained from the other half of the methylphenylvinylcarbinol molecule. The cleavage of methyl phenylvinylcarbinol, yielding acetophenone, has been observed only when it is reacted with 25% sulfuric acid. Under milder conditions, using a 15% aqueous-alcoholic sulfuric aicd (2:1 alcohol:water ratio) and three times as much of the aqueous-alcoholic sulfuric acid as of the methylphenylvinylcarbinol (at room temperature),

an allyl rearrangement of the methylphenylvinylcarbinol took place instead of cleavage, yielding the primary γ,γ-methylphenylallyl alcohol:

$$\begin{matrix} CH_3 \\ C_6H_5 \end{matrix}\!\!>\!COH - CH = CH_2 \longrightarrow \begin{matrix} CH_3 \\ C_6H_5 \end{matrix}\!\!>\!C = CH - CH_2OH,$$

i.e., a reaction similar to the one taking place when aqueous-alcoholic sulfuric acid is reacted with dimethylvinylcarbinol. Under our experimental conditions, we got approximately 50% of γ,γ-methylphenylallyl alcohol from the methylphenylvinylcarbinol used for the reaction. The residue consisted of a difficultly analyzable mixture of a primary and a tertiary alcohol, with a small quantity of a rather viscous liquid that was not subjected to further analysis. The primary alcohol was identified by several of its physical constants and was hydrogenated catalytically with platinum black; this yielded a saturated γ-phenylbutyl alcohol, which was then oxidized with a chromic acid mixture to produce β-phenylbutyric acid. Analysis of the silver salts of the synthesized acid showed that oxidation apparently resulted in forming a mixture of phenylbutyric and benzoic acids. We were unable to isolate the pure silver phenylbutyrate. The increased exaltation of the γ,γ-methylphenylallyl alcohol (approx. 1.5) is apparently due to the presence of conjugated double bonds, which do not exist in the methylphenylvinylcarbinol.

When 25% aqueous sulfuric acid was reacted with methylbenzylvinylcarbinol (120-122° fraction at 22 mm), we recovered a mixture that boiled in the 98-150° (10 mm) range. Four narrower fractions were isolated from this mixture. Analysis of all four fractions - for their percentages of carbon and hydrogen, their molecular refraction, and their molecular weight - indicated that their formula was $C_{11}H_{14}O$, i.e., that of the initial methylbenzylvinylcarbinol. The wide boiling-point range compels us to assume, however, that the mixture obtained by the action of sulfuric acid upon methylbenzylvinylcarbinol also contains the product of the latter's isomerization, γ,γ-methylbenzylallyl alcohol. All the fractions rapidly decolorized an aqueous solution of permanganate in the cold. No ketone was found in any of the fractions. In this case, apparently, the action of sulfuric acid does not cause ketone decomposition such as we observed under identical conditions for methylphenylvinylcarbinol, the only reaction taking place being an allyl rearrangement:

$$C_6H_5 - CH_2 - \underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}(OH) - CH = CH_2 \longrightarrow C_6H_5 - CH_2 - \underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}} = CH - CH_2OH$$

When methylbenzylvinylcarbinol was boiled for 10 hours with 25% sulfuric acid, we recovered a substance that boiled over a very wide range, from 79° to 168° (9 mm). Analysis of the first fraction indicated that this apparently was an unsaturated diene hydrocarbon; the composition of the third fraction rather resembled that of the initial alcohol. A test for carbonyl compounds was negative. The higher percentage of carbon and hydrogen in the first fraction justified the assumption that the action of sulfuric acid upon the hot reaction mixture causes partial detachment of water, giving rise to diene hydrocarbons, which we did not subject to further analysis. The absence of methylbenzylketone in the mixture indicates that methylbenzylvinylcarbinol does not undergo ketone decomposition even when heated, and that its behavior toward sulfuric acid is closer to that of dimethylvinylcarbinol than to that of methylphenylvinylcarbinol.

## EXPERIMENTAL

Action of aqueous sulfuric acid upon methylphenylvinylcarbinol. 25 g of methylphenylvinylcarbinol (98-100° at 10 mm) was mixed with 250 ml of 25% sulfuric acid. The mixture was agitated at 9° for 5 days (40 hours). Then the layers were separated. The top layer was washed with an aqueous soda solution and desiccated with

potash. The lower layer was extracted with ether. After being washed and desiccated with potash, the ether extract was added to the top layer. After the ether had been driven off, the product was distilled at reduced pressure, the following fractions being collected (at 7 mm): I - 73-80°, 0.7 g; and II - 80-100°, 5.7 g; the tarry residue in the flask totaled 13.6 g.

Redistillation of Fraction II (at 8 mm) yielded: I: 2.1 g at 82-90°; and II: 1.0 g at 90-100°.

The 82-90° (8 mm) fraction yielded a semicarbazone precipitate with semicarbazide; m.p. 182-184° (from alcohol). A test sample mixed with acetophenone semicarbazone fused at 180-181°. Treatment with ammoniacal silver nitrate produced a silver mirror. 1.6 g of this fraction was oxidized with moist silver nitrate. Then the mixture was extracted with ether. The ether was driven off. This left 0.75 g of an oily liquid with the odor of acetophenone. The semicarbazone of this liquid was prepared, fusing at 194-195° (from alcohol). A test sample mixed with acetophenone semicarbazone exhibited no depression. The residue of silver salts was oxidized with sulfuric acid and extracted with ether. Driving off the ether left behind a crystalline acid that fused (after some sublimation) at 119-120°. A test sample mixed with benzoic acid (m.p. 121°) fused at 120-121°. Thus, the mixture obtained was shown to contain acetophenone and a small amount of benzoic acid.

Action of aqueous-alcoholic sulfuric acid upon methylphenylvinylcarbinol. 20 g of methylphenylvinylcarbinol (93-94° fraction at 8 mm) was dissolved in 40 ml of 96% ethyl alcohol, and 20 ml of 25% sulfuric acid was added to the mixture. The mixture, which was transparent at first, soon grew cloudy, and then a layer was formed on top. The next day the layers were separated, top one being diluted with ether, washed with a potash solution, desiccated with calcined potash, and distilled. Distillation (at 8 mm) yielded the following fractions: I: 5.8 g at 99-113°; and II: 8.0 g at 113-115°; the viscous residue in the flask totaled 4.4 g.

Double redistillation of Fraction II yielded 1.2 g of a substance that boiled at 105-107° (5 mm).

Analysis of the fraction: $d_4^{22}$ 0.9696; $n_\alpha^{22}$ 1.52866; $MR_\alpha$ 47.03.
$C_{10}H_{12}OF_4$. Calculated: $MR_\alpha$ 45.50.

0.0943 g substance: 0.2802 g $CO_2$; 0.0717 g $H_2O$.
0.0858 g substance: 0.2555 g $CO_2$; 0.0654 g $H_2O$.
Found %: C 81.04, 81.14; H 8.51, 8.53.
$C_{10}H_{12}O$. Calculated %: C 81.02; H 8.17.
0.2010 g substance; 18.96 g benzene: $\Delta t$ 0.360°.
Found: M 152.5.
$C_{10}H_{12}O$. Calculated: M 148.1.

Hydrogenation of the 105-107° (5 mm) fraction. Hydrogenation was carried out in S.V.Lebedev's apparatus. 2.3 g of the substance; 0.5 g of platinum black; and 50 ml of absolute ethyl alcohol. Theoretically required (2H): 348 ml hydrogen. Absorbed: 350 ml hydrogen (376 ml at 15° and 744.8 mm). Ethylenic alcohol found: 100.6%.

Driving off the alcohol left behind 1.1 g of an oily liquid that did not decolorize an aqueous permanganate solution and distilled at 92-94° (4 mm).

$d_4^{20}$ 0.9535; $n_\alpha^{20}$ 1.49071; $MR_\alpha$ 46.52.
$C_{10}H_{14}OF_2$. Calculated: $MR_\alpha$ 45.998.

Oxidation of the 105-107° (5 mm) fraction. 1.1 g was oxidized under the conditions recommended for isoamyl alcohol [10]. After oxidation, the solution was diluted with water and distilled with steam. An oil distilled over that

did not produce a silver mirror and exhibited a faintly acid reaction. We were unable to prepare a silver salt of the acid distillate.

The residue left after the volatile parts had been driven off was diluted with water and extracted with ether; the ether extract was desiccated with calcined sodium sulfate, after which the ether was driven off and the acid residue converted into a silver salt.

Analysis of the silver salt.

Fraction I 0.0705 g substance: 0.0312 g Ag.
Fraction II 0.1340 g substance: 0.0611 g Ag.
Found %: Ag 44.38, 45.59.
$C_{10}H_{11}O_2Ag$. Calculated %: Ag 39.85.
$C_7H_5O_2Ag$. Calculated %: Ag 47.17.

The acid residue therefore apparently consisted of a mixture of benzoic and β-phenylbutyric acids.

Action of sulfuric acid upon methylbenzylvinylcarbinol.* 18 g of methylbenzylvinylcarbinol (b.p. 98-100° at 10 mm) was added to 180 ml of 25% sulfuric acid. The mixture was agitated for 45 hours at room temperature (15-18°). Then the top layer was removed, and the bottom layer was extracted with ether. The ether extract was poured into the top layer, which was then washed with soda and desiccated with potash. The ether was driven off, and the residue was fractionated. The following fractions were collected (at 10 mm): I – 3.6 g at 98-100°; and II – 4.0 g at 106-130°; the viscous residue in the distilling flask totaled 2.5 g.

Analysis of Fraction I: $d_4^{20}$ 1.0030; $n_\alpha^{20}$ 1.52567; $MR_\alpha$ 49.79.
$C_{11}H_{14}OF_4$. Calculated: $MR_\alpha$ 50.097.
0.1093 g substance: 13.63 g benzene; Δt 0.270.
Found: M 152.
$C_{11}H_{14}O$. Calculated: M 162.

Analysis of Fraction II: $d_4^{20}$ 0.9988; $n_\alpha^{20}$ 1.54686; $MR_\alpha$ 49.77.
$C_{11}H_{14}OF_4$. Calculated: $MR_\alpha$ 50.097.

Redistillations of Fractions I and II yielded a substance with a b.p. of 113-114° (20 mm); analysis of this substance for carbon and hydrogen gave the following results:

0.0950 g substance: 0.2824 g $CO_2$; 0.0713 g $H_2O$.
0.0992 g substance: 0.2965 g $CO_2$; 0.0722 g $H_2O$.
Found %: C 81.06, 81.51; H 8.40, 8.14.
$C_{11}H_{14}O$. Calculated %: C 81.48; H 8.64.

Analysis of Fraction III: $d_4^{20}$ 0.9870; $n_\alpha^{20}$ 1.52317; $MR_\alpha$ 50.13.
$C_{11}H_{14}OF_4$. Calculated: $MR_\alpha$ 50.097.
0.0528 g substance: 12.49 g benzene: Δt 0.130.
Found: M 166.
$C_{11}H_{14}O$. Calculated: M 162.

Subsequent distillation yielded a narrower fraction that boiled at 120-124° (17 mm); analysis of this fraction for carbon and hydrogen gave the following results:

0.0971 g substance: 0.2891 g $CO_2$; 0.0742 g $H_2O$.
0.0966 g substance: 0.2877 g $CO_2$; 0.0761 g $H_2O$.
Found %: C 81.21, 81.23; H 8.55, 8.81.
$C_{11}H_{14}O$. Calculated %: C 81.48; H 8.64.

All three fractions rapidly decolorize an aqueous permanganate solution in the cold and do not react with semicarbazide.

*Performed by the student V. A. Shlyakova.

Thus, the results of analysis of all three fractions fit the formula $C_{11}H_{14}O$; but the broad boiling-point range indicates that this is a mixture of a primary and a tertiary alcohol. Fraction I consisted principally of methylbenzylvinylcarbinol, while Fraction III was γ,γ-methylbenzylallyl alcohol.

Determination of the molecular weight of the viscous residue indicated that it apparently consists of a mixture of the dimer and trimer of methylbenzylvinylcarbinol or the product of the latter's dehydration. The only product recovered after oxidation was benzoic acid. This polymer was not subjected to further analysis.

Action of sulfuric acid upon methylbenzylvinylcarbinol when heated. 8 g of methylbenzylvinylcarbinol was heated for 10 hours with 80 ml of 25% sulfuric acid. After heating was over, the mixture was given the same treatment as in the preceding experiment and then distilled. The following fractions were recovered (at 9 mm): I – 0.77 g at 75-82°; II – 0.78 g at 82-88°; and III – 2.78 g at 88-108°; the residue was a viscous polymer.

Analysis of Fraction I: $d_4^{20}$ 0.9572.

0.1294 g substance: 12.37 g benzene; Δt 0.410.
Found: M 131.
$C_{11}H_{12}$. Calculated: M 144
0.1017 g substance: 0.3302 g $CO_2$; 0.0724 g $H_2O$.
Found %: C 88.55; H 7.97.
$C_{11}H_{12}$. Calculated %: C 91.66; H 8.33.
$C_{11}H_{14}O$. Calculated %: C 81.48; H 8.64.

Redistillation of Fraction III yielded a substance with a b.p. of 84-85° (5 mm) and $d_4^{20}$ 0.9724, which was analyzed as follows:

0.1466 g substance: 15.14 g benzene: Δt 0.514.
Found: M 158.
$C_{11}H_{14}O$. Calculated: M 162.
0.0938 g substance: 0.2878 g $CO_2$; 0.0739 g $H_2O$.
Found %: C 83.68; H 8.81.
$C_{11}H_{14}O$. Calculated %: C 81.48; H 8.64.

All the fractions rapidly decolorized an aqueous permanganate solution in the cold and did not react with semicarbazide. Apparently, they consist largely of a mixture of a diene hydrocarbon and the initial alcohol, which we were unable to separate more carefully owing to the small quantity of products recovered.

## SUMMARY

1. The action of dilute sulfuric acid (25%) upon methylphenylvinylcarbinol and methylbenzylvinylcarbinol has been investigated.

2. When 25% aqueous sulfuric acid is reacted with methylphenylvinylcarbinol, the latter is cleaved, forming acetophenone and a polymer product.

3. When 13% aqueous-alcoholic sulfuric acid is reacted with methylphenylvinylcarbinol, no ketone decomposition is observed, an allyl rearrangement taking place to form a γ,γ-methylphenylallyl alcohol hitherto not described in the literature.

4. When 25% aqueous sulfuric acid is reacted with methylbenzylvinylcarbinol, the only reaction observed is the latter's allyl rearrangement into γ,γ-methylbenzylallyl alcohol.

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* Cf CB translation p. 1285 ff.

# THE SYNTHESIS OF METHYLETHYLALLYL CARBINOL AND ITS TRANSFORMATIONS WHEN ACTED UPON BY SULFURIC ACID

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The dialkylallylcarbinols have long attracted the attention of research workers; their possession of a third hydroxyl group and a double bond makes them extremely reactive and capable of various isomeric transformations. Their dehydration is of special interest, and it has been the research topic of several scientists: A.M.Zaitsev [1], Lyubarsky [2], and S.N.Reformatsky [3], and more recently, Escourrou [4], Y.M.Slobodin [5], A.D.Petrov [6], and others. But in many instances the structure of the hydrocarbons formed has been established only recently, as the initial researches on these alcohols by A.M.Zaitsev and his pupils were carried out at a time when chemists did not yet have at their disposal two fundamental methods of determining the structure of unsaturated compounds: The E.E.Wagner method of oxidation by a potassium permanganate solution and the ozonation method. In his 1938 research on the action of sulfuric and oxalic acids upon dimethylallylcarbinol, Slobodin demonstrated that this results in the formation of a hydrocarbon that condenses with maleic anhydride and, hence, contains a conjugated system of double bonds, whereas the authors who had studied this reaction previously had held that the resulting hydrocarbon had isolated double bonds: $CH_2=C(CH_3)-CH_2-CH=CH_2$, 2-methylpentadine-1,4.

Slobodin obtained similar results in his study of the dehydration of diethyl-, dipropyl-, and diisopropylallylcarbinols: in every case he recovered a hydrocarbon with conjugated double bonds, with more or less traces of hydrocarbons with isolated bonds.

A.D.Petrov considers that the dehydration of dialkylallylcarbinols always occurs at one of the saturated radicals; the synthesis of hydrocarbons with conjugated double bonds by reaction with sulfuric acid when the dehydration reaction affects the allyl radical is due to the isomerizing action of sulfuric acid. He believes that all acid agents can bring about isomerization of the hydrocarbons produced by dehydration. That is why he undertook a study of the dehydration of tertiary alcohols of the $C_nH_{2n-1}OH$ series over alumina, which yielded chiefly hydrocarbons with isolated double bonds.

Owing to the proximity of the alcohol group to three different aliphatic radicals, the dehydration of dialkylallylcarbinols by sulfuric acid is a simple reaction only in rare instances; the experimental conditions may promote or retard one direction or another taken by the reaction, and in some cases one particular isomer will be recovered almost exclusively. It seems to us that

this may be the reason for the fact that various researchers have ascribed different structures to the hydrocarbons they synthesized by reacting sulfuric acid on the identical allyl alcohol. Moreover, the radicals comprising the alcohol will, of course, likewise affect the course of the dehydration. Lastly, whenever dehydration is effected with a reagent like sulfuric acid, isomeric transformations of the synthesized hydrocarbons as well as of the initial alcohols may take place.

Using methylphenyl- and diphenylallylcarbinols as examples, we have demonstrated [7] that, in addition to all the foregoing transformations, the reaction of allyl alcohols with sulfuric acid may also result in the decomposition of the molecule of the initial alcohol, giving rise to the corresponding ketone and an unsaturated hydrocarbon.

Inasmuch as no one had previously observed such a conversion of allyl alcohols, we desired to check whether such decomposition products were formed, even if in negligible amounts, when sulfuric acid was reacted with tertiary allyl alcohols containing two saturated aliphatic radicals. The alcohol chosen for this test was methylethylallylcarbinol.

Methylethylallylcarbinol was first synthesized by N.Zaitsev [8] from methyl ethyl ketone and allyl iodide in the presence of zinc, with a yield of 17%. In 1935 Milas and McAlevy [9] synthesized it by reacting allyl chloride and allyl bromide and methyl ethyl ketone with magnesium. Using the method suggested by Yavorsky [10] for the synthesis of allyl alcohols, i.e., carrying out the reaction in a single phase without the prior preparation of an allylmagnesium halide, and employing specially activated magnesium, the authors secured a yield of 42% of methylethylallylcarbinol. In our research we used unactivated magnesium shavings, and the synthesis was performed by the Yavorsky method, in a single phase. This yielded 33% of methylethylallylcarbinol and approximately 5-6% of an isomeric alcohol whose boiling point was 26° higher than that of methylethylallylcarbinol. Exactly when did the isomerization of the methylethylallylcarbinol occur During the formation of the organomagnesium coordination compound or during its decomposition by water and sulfuric acid To check the latter assumption the methylethylallylcarbinol was agitated with dilute sulfuric acid in a "shaker" at room temperature for several hours; the alcohol was recovered unchanged in practically the quantitative yield. Thus no isomerization took place under these conditions. We were therefore left with the assumption that isomerization occurs during the synthesis of the methylethylallylcarbinol. The papers by the authors cited above make no mention of the formation of a higher-boiling alcohol under the experimental conditions employed by them.

The structure of the synthesized isomeric alcohol was proved by its oxidation with potassium permanganate, yielding methyl ethyl ketone and acrylic acid. These products can come only from a primary alcohol, 3-methylhexen-3-ol-6.

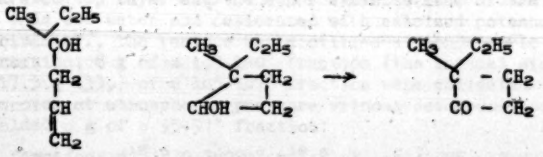
$$CH_3CH_2\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}} = CH - CH_2 - CH_2OH \rightarrow CH_3CH_2COCH_3 + HOOC - CH_2 - CH_2OH$$

$$HOCH_2 - CH_2 - COOH \rightarrow CH_2 = CH - COOH_2.$$

As we see it, the formation of this alcohol from methylethylallylcarbinol is best explained by the intramolecular isomeric transformation of the tertiary alcohol, accompanied by a shift of the hydroxyl group to the gamma position. The shift of the hydroxyl group to the gamma position is extremely interesting, and we are the first to have observed it. There are references in the literature to shifts of hydroxyl groups to more distant positions, but only when the molecule contained conjugated double bonds [11]. There are no known examples of such shifts

for alcohols containing allyl radicals.

It may be appropriate to mention one interesting transformation at this point, observed by us during the synthesis of methylethylallylcarbinol. We set up an experiment aimed at synthesizing methylethylallylcarbinol under the usual conditions of organomagnesium synthesis, i.e., in two phases rather than in one, adding a solution of methyl ethyl ketone to the initially synthesized allylmagnesium bromide. The resulting alcohol yield was considerably lower; part of the magnesium remained unreacted, and a diallyl hydrocarbon was formed. Another experiment, set up to synthesize methylethylallylcarbinol under these conditions, yielded quite unexpected results. All the synthesized products distilled at temperatures below 120° (the boiling point of methylethylallylcarbinol is 138-140°). They contained a diallyl compound, the methyl ethyl ketone that did not enter into the reaction, and a substance with a b.p. of 120-122°, with a characteristic camphor odor, containing no halogen or carbonyl group and not decolorizing a potassium permangante solution or bromine in chloroform, which was recovered as the principal reaction product (20%), which indicated that it did not contain a three-membered polymethylene ring. Supposing that this was an isomeric conversion of the methylethylallylcarbinol with a shift of the hydroxyl group to the beta position, followed by the closing of a four-membered ring and the formation of methylethylcyclobutanol, we oxidized the resulting product with nitric acid by the Demyanov method [2], expecting to obtain methylethylcyclobutanone:



But under these oxidation conditions the molecule was even more thoroughly decomposed, oxalic acid being formed. The experiment involving the synthesis of the substance with a b.p. of 120-122° was repeated several times under identical conditions, with the same samples of reagents as well as with different ones, but in no other instance did we recover a trace of this product; the reaction yielded the diallyl compound and methylethylallylcarbinol. The interesting course of the reaction referred to above was probably due to the presence of minute quantities of some substance that acted as a catalyst and caused the reaction to take that turn. Owing to a shortage of the material we were unable, unfortunately, to demonstrate the structure of the interesting product synthesized, but we feel obliged to mention the possibility of the reaction taking this course during the synthesis of methylethylallylcarbinol.

The methylethylallylcarbinol we synthesized was heated with 25% sulfuric acid. From the reaction products we recovered 33% of an alcohol whose constants were wholly identical with those of the primary alcohol recovered in the organomagnesium synthesis, together with a small quantity of a lower-boiling fraction that distilled in a 15° range and had constants that agreed with those of the corresponding diene hydrocarbon. We were unable to detect the presence of a carbonyl group in the products of the lower-boiling fraction, no ketone decomposition took place, and the reaction chiefly involved the isomerization of the tertiary alcohol to a primary one, accompanied by slight dehydration of the initial alcohol.

## EXPERIMENTAL

Synthesis of methylethylallylcarbinol. 50 ml of absolute ether was poured

over 30 g of magnesium. To start the reaction going some methyl iodide was added, after which a mixture of 30 g of methyl ethyl ketone and 150 g of allyl bromide dissolved in 450 ml of absolute ether was added drop by drop during the space of 6 hours. After this was completed, stirring continued for another hour. The organomagnesium compound was decomposed with ice water and dilute sulfuric acid. The ether layer and extracts made from the aqueous layer were desiccated with $K_2CO_3$.

The product recovered by driving off the ether was distilled at atmospheric pressure, yielding 47 g (55%) of an alcohol with a b.p. of 138-140°. The residue in the distilling flask that did not pass over at atmospheric pressure was distilled at 9 mm. The product obtained, which was thus freed from a fairly large quantity of tar, was redistilled at atmospheric pressure, yielding 8 g (5.6%) of a substance with a b.p. of 165-167°.

138-140° fraction: $d_4^0$ 0.8641; $d_4^{22}$ 0.8410; $n_\alpha^{22}$ 1.4390; $MR_\alpha$ 35.45.
$C_7H_{14}OF$. Calculated: $MR_\alpha$ 35.38.

Literature data on methylethylallylcarbinol [8]: b.p. 139°; $d^0$ 0.8686; $d^{20}$ 0.8431.

165-167° fraction: $d_4^0$ 0.8648; $d_4^{20}$ 0.8497; $n_\alpha^{20}$ 1.4461.

Reaction of methylethylallylcarbinol with 25% sulfuric acid. 52 g of methylethylallylcarbinol was heated to boiling with 500 ml of 25% sulfuric acid for 1 hour. The separated top layer and the ether extracts made of the bottom layer were washed with soda and water and desiccated with calcined potash. After the ether had been driven off, the residue was distilled at atmospheric pressure. 2.5 g of a 90-105° fraction, 8 g of a 135-140° fraction (the initial alcohol recovered unchanged), and 17.5 g (33%) of a 165-167° fraction were collected. The residue that did not pass over at atmospheric pressure without decomposition was distilled at 8 mm; this yielded 5 g of a 55-97° fraction.

90-105° fraction: $d_4^{19.5}$ 0.7622; $n_\alpha^{19.5}$ 1.4367; $MR_\alpha$ 32.99.
$C_7H_{12}F_2$. Calculated: $MR_\alpha$ 33.36.

0.1558 g substance: 25.00 g benzene: $\Delta t$ 0.32°.
Found: M 94.1.
$C_7H_{12}$. Calculated: M 96.0.

135-140° fraction: $d_4^{20}$ 0.8554; $n_\alpha^{20}$ 1.4381; $MR_\alpha$ 35.72.
$C_7H_{14}OF$. Calculated: $MR_\alpha$ 35.38.

These constants are the same as those for the initial methylethylallyl carbinol.

165-167° fraction: $d_4^0$ 0.8661; $d_4^{18}$ 0.8515; $n_\alpha^{18}$ 1.4444; $MR_\alpha$ 35.88.
$C_7H_{14}OF$. Calculated: $MR_\alpha$ 35.38.

0.1115 g substance: 0.3016 g $CO_2$; 0.1203 g $H_2O$.
0.1396 g substance: 0.3747 g $CO_2$; 0.1482 g $H_2O$.
Found %: C 73.79, 74.19; H 12.07, 12.14.
$C_7H_{14}O$. Calculated %: C 73.68; H 12.28.

0.1838 g substance: 22.06 g benzene: $\Delta t$ 0.33°.
0.2093 g substance: 24.56 g benzene: $\Delta t$ 0.36°
Found: M 126.6, 120.8
$C_7H_{14}O$. Calculated: M 114.

The constants of this fraction are the same as those for the substance with a b.p. of 165-167° recovered during the synthesis of methylethylallylcarbinol.

Oxidation of the substance with a b.p. of 165-167°. Oxidation of 20 g of

the alcohol required 61 g of potassium permanganate to produce a permanant coloration. The precipitate of $MnO_2$ was filtered out, and the filtrate was steam distilled, ether extracts being made of the distillate. The $MnO_2$ precipitate was heated over a water bath with ether for 6 hours to extract the neutral products from it. Drying and driving off the ether yielded about 2 g of a substance that was treated with a semicarbazide solution. The resulting semicarbazone was recrystallized from alcohol; its m.p. was 137-137.5°. A test sample mixed with the known semicarbazone of methyl ethyl ketone exhibited no depression. The first drops of distillate that passed over in the steam distillation of the neutral products were treated with p-nitrophenylhydrazine. The resulting p-nitrophenylhydrazone exhibited no depression when mixed with the p-nitrophenylhydrazone of known methyl ethyl ketone.

The solution of salts obtained as the result of oxidation was evaporated over a water bath; after it had cooled, it was acidulated with dilute sulfuric acid. The resulting acids were extracted with ether, first manually and then in an extractor. Drying and driving off the ether resulted in the recovery of an acid with a b.p. of 132-137°, which had an acrid odor that reminded one of the odor of acetic acid, and decolorized a permanganate solution. The silver salt of the acid with a b.p. of 132-137° was prepared; it settled out as stellate crystals.

0.0836 g substance: 0.0506 g Ag.
0.0756 g substance: 0.0455 g Ag.
Found %: Ag 60.52, 60.41.
$C_3H_3O_2Ag$. Calculated %: Ag 60.33.

When we tried to prepare lead acrylate, it settled out as a viscous, transparent, gummy mass instead of as crystals; we had observed a similar phenomenon previously [13], but at that time had succeeded in converting this mass into a crystalline salt, consisting of typical fibrous needles. We were unable to accomplish this this time.

No oxalic acid was detected by the usual methods in the acid solution left after the acrylic acid had been separated out.

95-97° (8 mm) fraction: $d_4^0$ 0.8667; $d_4^{17}$ 0.8545; $n_\alpha^{17}$ 1.4778; $MR_\alpha$ 63.57. $C_{14}H_{24}F_2$. Calculated: $MR_\alpha$ 63.24.

0.3416 g substance: 20.61 g benzene: $\Delta t$ 0.455°.
Found: M 187.7.
$C_{14}H_{24}$. Calculated: M 192.

Hence, it may be stated that when methylethylallylcarbinol is heated with 25% sulfuric acid, the following reaction products were obtained:

1) 8 g (15%) of the initial alcohol: 2) 2.5 g (6%) of the hydrocarbon $C_7H_{12}$; 3) 9 g (20.5%) of its dimer $C_{14}H_{24}$; and 4) 17.5 g (34%) of the primary alcohol $C_7H_{14}O$.

Treatment of methylethylallylcarbinol with 20% sulfuric acid in the cold. 7.5 g of methylethylallylcarbinol was placed in a flask fitted with a ground-in stopper together with 90 ml of 20% $H_2SO_4$ and agitated for 20 hours in a "shaker". All the alcohol was recovered unchanged after the test.

Synthesis of methylethylallylcarbinol in two phases. 126 g of allyl bromide dissolved in 100 ml of ether was added to 24 g of magnesium covered with ether during the course of 2 hours. After the reaction was complete, 75 g of methyl ethyl ketone in 100 ml of ether was added to the ice-chilled allylmagnesium bromide. The organomagnesium compound was decomposed with ice water and dilute sulfuric acid. The ether layer decanted from the aqueous solution and the ether extracts made were desiccated with calcined potash. The magnesium that had not entered into reaction

was washed and dried; it weighed 6.5 g. The ether driven off from the extracts had a strong hydrocarbon odor and boiled at approximately 40° (the diallyl compound has a b.p. of 58-59°). Repeated redistillation yielded 25 g of methylethylallylcarbinol with a b.p. of 137-139°, a yield of 30% based on the magnesium consumed in the reaction. In another test made under exactly the same conditions, 18.5 g of a substance with a b.p. of 120-122° was recovered after the ether had been driven off and the reaction products were distilled.

120-122° fraction: $d_4^0$ 0.8402; $d_4^{6.5}$ 0.8390; $d_4^{20}$ 0.8291; $n_\alpha^{6.5}$ 1.4189; $MR_\alpha$ 34.31.

$C_7H_{14}O$. Calculated: $MR_\alpha$ 33.70.

## SUMMARY


1. It has been established that when methylethylallylcarbinol is reacted with sulfuric acid and heated, the reaction follows two courses: dehydration of the cohol, yielding a monomeric and dimeric hydrocarbon, and isomerization of the tiary alcohol to a primary one.

2. It has been established that the isomerization of methylethylallylcarbinol is accompanied by a shift of the hydroxyl group to the gamma position, the primary alcohol 3-methylhexen-3-ol-6 being formed.

3. The structure of the primary alcohol has been established by oxidizing it to form methyl ethyl ketone and acrylic acid.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# SYNTHESIS OF HYDROCARBONS

## IX. DIENE HYDROCARBONS IN THE SYNTHESIS OF OLEFIN HYDROCARBONS WITH CENTRALLY LOCATED DOUBLE BONDS

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In one of our previous reports [1] we described the reaction of 1,4-divinyl dichloride (1,4-dichloro-2-butene) with methylmagnesium bromide. With this reaction we were the first to show that unsaturated 1,4-dichlorides, in which both halogen atoms of the allyl type are under the activating influence of the same double bond behave like allyl chloride in reactions with organomagnesium compounds. For example, 1,4-divinyl dichloride reacts with methylmagnesium bromide to exchange both chlorine atoms for radicals of the organomagnesium compound, forming a trans alkene (3-hexene) with a centrally located double bond:

$$CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{+Cl_2} \underset{\displaystyle Cl}{\overset{}{CH_2CH{=}CH}}\underset{\displaystyle Cl}{\overset{}{CH_2}} \xrightarrow{+2CH_3MgBr} CH_3CH_2CH{=}CHCH_2CH_3.$$

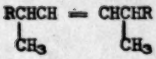
Inasmuch as 1,4-divinyl dichloride is a diprimary unsaturated 1,4-dichloride, we were interested in studying the behavior of disecondary unsaturated 1,4-dichlorides in this reaction.

With this in view, this paper is a report on the reaction of 1,4-dipropenyl dichloride (2,5-dichloro-3-hexene) with methyl- and ethylmagnesium bromides. It has been established that in 1,4-dipropenyl dichloride both of the chlorine atoms possess mobility and (like the chlorine atoms in 1,4-divinyl dichloride) can be replaced by the radicals of an organomagnesium compound, giving rise to trans alkenes with a centrally placed double bond:

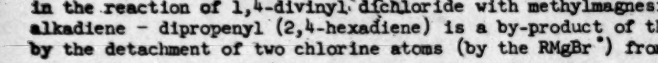
$$CH_3CH{=}CH{-}CH{=}CHCH_3 \xrightarrow{+Cl_2} CH_3\underset{\displaystyle Cl}{\overset{}{CH}}CH{=}CH\underset{\displaystyle Cl}{\overset{}{CH}}CH_3 \xrightarrow{+2RMgBr} R\underset{\displaystyle CH_3}{\overset{}{CH}}CH{=}CH\underset{\displaystyle CH_3}{\overset{}{CH}}R$$

When 1,4-dipropenyl dichloride was reacted with methylmagnesium bromide, 2,5-dimethyl-3-hexene was synthesized (the yield was 20% of the theoretical), and when it was reacted with ethylmagnesium bromide, 3,6-dimethyl-4-octene was synthesized (the yield being 25% of the theoretical).

The availability of the initial alkadiene (dipropenyl) and the simplicity of all the reactions justify our considering this a new method for the synthesis of iso alkenes with centrally located double bonds, such as:



When 1,4-dipropenyl dichloride is reacted with organomagnesium compounds (as in the reaction of 1,4-divinyl dichloride with methylmagnesium bromide), the initial alkadiene - dipropenyl (2,4-hexadiene) is a by-product of the reaction, being formed by the detachment of two chlorine atoms (by the RMgBr*) from the initial dichloride:



## EXPERIMENTAL

### 1. Chlorination of Dipropenyl (2,4-Hexadiene)

The chlorination of dipropenyl, investigated for the first time in our research, was effected under varying conditions (temperature and solvent). The method that produced the highest yield of the dichloride is set forth below.

The dipropenyl (10 g) was chlorinated in an ether solution (30-40 ml), the reaction vessel being chilled by a snow-and-salt mixture. The reaction was considered to be complete when the increase in weight of the reaction mixture had reached the theoretical value, based on the addition of two chlorine atoms to the dipropenyl molecule. The reaction vessel was balanced on scales to make it possible to observe the increase in weight and determine the end of the reaction. The chlorine current was a gentle one to prevent rapid heating and the liberation of hydrogen chloride as well as the carrying off of the hydrocarbon and the ether by the current of gas. The absorption of chlorine was nearly uniform, with some slight acceleration toward the end of the experiment. The requisite increase in the weight of the dipropenyl from 8 g to 10 g was attained after 50 to 60 minutes had elapsed. After the ether had been driven off and the residue had been distilled in vacuum (with a tall dephlegmator), we recovered 1,4-dipropenyl dichloride (2,5-dichloro-3-hexene), possessing the following constants:

B.p. 78.5-79° (37 mm); $n_D^{20}$ 1.4710; $d_4^{20}$ 1.0692; $MR_D$ 40.00.
$C_6H_{10}Cl_2$ F. Calculated: $MR_D$ 39.2; $E_{MD}$ 0.80.

6.784 mg substance: 11.866 mg $CO_2$; 3.643 mg $H_2O$.
4.278 mg substance: 7.520 mg $CO_2$; 2.313 mg $H_2O$.
Found %: C 47.51, 47.48; H 5.98, 6.01.
$C_6H_{10}Cl_2$. Calculated %: C 47.30; H 6.05.

The dichloride yield was 70% of the theoretical. In all succeeding tests (eleven in all) made with this method the same yield was attained.

The dipropenyl dichloride was ozonated in order to determine its structure. Only one acid was isolated from the ozonation products, its constants and analysis indicating that it was α-chloropropionic acid. The acid was distilled at 184° (760 mm) and had a $n_D^{20}$ 1.4320.

10.250 mg substance: 12.52 mg $CO_2$; 4.53 mg $H_2O$.
8.505 mg substance: 10.41 mg $CO_2$; 3.67 mg $H_2O$.
Found %: C 33.33, 33.40; H 4.92, 4.80.
$C_3H_5O_2Cl$. Calculated %: C 33.21; H 4.61.

Literature data: B.p. 75° (13 mm); $n_D^{20}$ 1.4341 [2].

*The mechanism of this side reaction has been established in our subsequent investigations (cf our next report).

## 2. Reaction of 1,4-Dipropenyl Dichloride (2,5-Dichloro-3-hexene) with Methylmagnesium Bromide

An ether solution of 1,4-dipropenyl dichloride (51 g) was added with constant stirring to methylmagnesium bromide (128 g of methyl bromide and 32 g of magnesium). After all the dichloride had been added, the reaction mixture was heated for 1 hour over a water bath and left to stand overnight; the next day heating was resumed for another 12 hours. Decomposition was effected with dilute acetic acid (10%). The ether extract was washed until its reaction was neutral and then dried with calcium chloride, after which the ether was driven off and the residue was fractionated over sodium (into a tower with 30 theoretical trays). This yielded 7 g (30% of the theoretical yield) of 2,5-dimethyl-3-hexene, with a b.p. of 103.5°, (750 mm) (cf Sect. 3). In addition to the 2,5-dimethyl-3-hexene, 14 g of the initial diene hydrocarbon - dipropenyl (2,4-hexadiene) - was recovered from the reaction products during distillation into the tower. Hence, 50% of the dipropenyl dichloride placed in reaction was consumed in forming dipropenyl. The dipropenyl was identified by its constants: b.p. 82° (756 mm); $n_D^{20}$ 1.4530; $d_4^{20}$ 0.7212; and by the melting point of its addition compound with maleic anhydride (93-94°).

Literature data: Levina, Derendyaeva, and Fainzilberg [3] - b.p. 80-82° (740 mm); $n_D^{20}$ 1.4518; $d_4^{20}$ 0.7184: Henne and Chanan [4] - b.p. 82°; $n_D^{20}$ 1.4535; $d_4^{20}$ 0.7242: Diels and Alder [5] - m.p. of the addition product with maleic anhydride 93-94°.

## 3. Analysis of the Hydrocarbon with B.P. of 103.5° - 2,5-Dimethyl-3-hexene

The hydrocarbon with a b.p. of 103.5° - the product of the reaction of 1,4-dipropenyl dichloride with methylmagnesium bromide, to which the structure of 2,5-dimethyl-3-hexene could have been ascribed by virtue of the method of its synthesis - was redistilled over sodium (into a tower with 30 theoretical trays); it contained no traces of halogens and possessed the following constants:

B.p. 103-103.5° (756 mm); $n_D^{20}$ 1.4100; $d_4^{20}$ 0.7122; $MR_D$ 39.04.

$C_8H_{16}$. Calculated: $MR_D$ 38.67.

4.220 mg substance: 13.258 mg $CO_2$; 5.391 mg $H_2O$.

3.250 mg substance: 10.215 mg $CO_2$; 4.185 mg $H_2O$.

Found %: C 85.70, 85.75; H 14.20, 14.32.

$C_8H_{16}$. Calculated %: C 85.71; H 14.28.

Literature data: The synthesis of 2,5-dimethyl-3-hexene is not described in the literature; but in Egloff's handbook the constants of this hydrocarbon are cited from a dissertation by Reid [7]: b.p. 102-102.1° (710 mm); $n_D^{20}$ 1.4030; $d_4^{20}$ 0.7124.

Bromination of 2,5-dimethyl-3-hexene. 2,5-Dimethyl-3-hexene was brominated in a snow-chilled ether solution. The 2,5-dimethyl-3,4-dibromohexane produced possessed the following constants:

B.p. 109°(19 mm); $n_D^{20}$ 1.5058; $d_4^{20}$ 1.5034; $MR_D$ 53.76.

$C_8H_{16}Br_2$. Calculated: $MR_D$ 53.77.

2,5-Dimethyl-3,4-dibromohexane is not described in the literature.

Optical analysis of 2,5-dimethyl-3-hexene. The combined scattering spectrum of 2,5-dimethyl-3-hexene was photographed with a Steinheil three-prism glass spectrograph with a linear dispersion $\frac{dv}{dl}$ = 0.017 mm/cm$^{-1}$. The line 22938 cm$^{-1}$ was used for excitation. A solution of potassium nitrite was used as the light filter. The spectra were photographed on an Eastman Kodak P-0 plate. The frequencies of the lines in the combined light-scattering spectrum were measured by means of linear interpolation between the two closest lines of the iron spectrum, photographed at the same time by means of a Hartmann diaphragm. The combined light-scattering

spectrum of 2,5-dimethyl-3-hexene was investigated in the frequency range of 0 to 3000 $cm^{-1}$. The intensity of the spectrum lines was estimated visually. The results of measuring the frequencies of the combined light-scattering spectrum of 2,5-dimethyl-3-hexene were as follows:

269* (2); 276-294* (2); 337 (2); 373 (0.75); 387* (0.5); 411 (0.9); 434 (1.5); 460 (3.5); 467* (0.5); 500** (3); 546* (0.5); 612* (0); 671* (1); 702** (1); 770 (1.5; B); 804 (3.5); 831 (3); 855 (3.5); 887 (1); 920 (3.5); 956 (3); 985** (2); 1022 (0); 1040 (2;B); 1104* (5;B); 1170 (2.2;B); 1254 (0.7; B); 1296-1302 (10; B); 1382 (2.5); 1440-1460 (10; B) 1571(1.4); 1668 (20); 2876** (3.5); 2942 (0.75); 2965 (1.5); 3051** (0.7); 3128 (0.5).

The presence of the intense frequency 1668 $cm^{-1}$ in the spectrum indicated that the 2,5-dimethyl-3-hexene we had synthesized was the pure trans form. No traces of the cis form were detected.

4. Reaction of 1,4-Dipropenyl Dichloride with Ethylmagnesium Bromide

The reaction between 1,4-dipropenyl dichloride (60 g) and ethylmagnesium bromide (168 g of ethyl bromide and 32 g of magnesium) was carried out under the same conditions as those used for the methylmagnesium bromide (cf Sect. 2). Fractional distillation of the reaction products over sodium (into a tower with 30 theoretical trays), after the usual treatment of the reaction mixture and the expulsion of the ether from the washed and desiccated ether extract, yielded a hydrocarbon with a b.p. of 149.5-150° (760 mm) – 3,6-dimethyl-4-octene. The yield of the hydrocarbon totaled 14 g or 25% of the theoretical (cf Sect. 5).

Besides the 3,6-dimethyl-4-octene, the reaction products also yielded the initial diene hydrocarbon – dipropenyl (2,4-hexadiene), which was identified [after distillation into a tower] by its constants [b.p. 82° (750 mm); $n_D^{20}$ 1.4534; $d_4^{20}$ 0.7214] and by the melting point of its addition product with maleic anhydride (93-94°).

5. Analysis of the Hydrocarbon with B.P. of 149.5-150° -3,6-Dimethyl-4-octene

The synthesized 3,6-dimethyl-4-octene was redistilled over sodium (into a tower with 30 theoretical trays); it contained no traces of halogen and possessed the following constants:

B.p. 149.5-150° (760 mm); $n_D^{20}$ 1.4205; $d_4^{20}$ 0.7702; $MR_D$ 48.00.
$C_{10}H_{20}$. Calculated: $MR_D$ 47.9.

3.685 mg substance: 11.580 mg $CO_2$; 4.735 mg $H_2O$.
4.255 mg substance: 13.370 mg $CO_2$; 5.449 mg $H_2O$.
Found %: C 85.70, 85.69; H 14.38, 14.35.
$C_{10}H_{20}$. Calculated %: C 85.71; H 14.29.

Literature data. In the Gubelmann and Spiegler patent [8] the constants of 3,6-dimethyl-4-octene, synthesized by partial hydrogenation of 3,4,5,6-tetramethyldivinylacetylene, are given as follows: b.p. 153-156°; $n_D^{20}$ 1.4213; $d_4^{20}$ 0.737; $MR_D$ (based on a $n_D^{20}$ 1.4263) 48.79. $C_{10}H_{20}$. Calculated: $MR_D$ 47.9. Apparently, the hydrocarbon synthesized by the foregoing authors was not sufficiently pure.

Oxidation of 3,6-dimethyl-4-octene. The hydrocarbon was oxidized with a 2% aqueous solution of potassium permanganate in the cold, in the presence of manganese

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*The following notation has been used to indicate combined lines: b-wide band; B-background. The spectra were photographed twice, the frequency values being almost identical for the two spectrograms. When a slight difference occurred, the mean of two measurements was taken. The asterisks denote lines detected on only one of the spectrograms.

**The spectrum line coincides with a line of the mercury-vapor lamp.

sulfate. The oxidation product proved to be methylethylacetic acid, with a b.p. of 173-175°.

5.060 mg substance: 10.890 mg $CO_2$; 4.085 mg $H_2O$.
7.620 mg substance: 16.410 mg $CO_2$; 6.795 mg $H_2O$.
Found %: C 58.7, 58.73; H 9.85, 9.91.
$C_5H_{10}O_2$. Calculated %: C 58.82; H 9.8.

Literature data: Seib [9]: b.p. 173-174.5°; Asahina [10]; b.p. 176°.

Bromination of 3,6-dimethyl-4-octene. The hydrocarbon was brominated in a snow-chilled ether solution. The synthesized 3,6-dimethyl-4,5-dibromooctane possessed the following constants:

B.p. 137° (32 mm); $n_D^{20}$ 1.5000, $d_4^{20}$ 1.3800; $MR_D$ 63.95.
$C_{10}H_{20}Br_2$. Calculated: $MR_D$ 63.91.

3,6-dimethyl-4,5-dibromooctane has not been described in the literature.

Optical analysis of 3,6-dimethyl-4-octene. The spectrum was photographed under the same conditions as those used for the spectrum of 2,5-dimethyl-3-hexene (cf. Sect. 3). The results of measuring the frequencies of the combined light-scattering spectrum of 3,6-dimethyl-4-octene were as follows:

224 (1.2; B; b); 276 (1; B); 310 (2.5; B); 344 (1.8; B); 383 (0.2); 433 (1.8); 460 (1.5; b); 470 (2); 530 (0.3); 587 (0.3; B); 644 (0.3); 769(1.5); 795(1.5); 822(1.2); 845 (5; B); 863 (0.5); 909 (1; b); 932 (1.5; B) 970 (0.3; b); 987 (3; 5); 1012 (1.5); 1040 (2; B); 1090 (3); 1144-1170 (2; B); 1218 (1.2); 1258 (0; b); 1270 (1.5); 1301 ((4; B); 1340 (1.2); 1382 (1); 1440-1460 (10; B); 1668 (9); 2822 (0.5); 2863 (1); 2877 (4; B); 2903 (1; B); 2939 (1.5); 2967 (2.5; B); 3003 (1).

The presence of the frequency 1668 $cm^{-1}$ in the spectrum indicates that the 3,6-dimethyl-4-octene was the pure trans form.

## SUMMARY

1. It has been shown, for the first time, that a disecondary unsaturated 1,4-dichloride (1,4-dipropenyl dichloride) can react with organomagnesium compounds, forming trans alkenes with a centrally located double bond.

2. The reaction of 1,4-dipropenyl dichloride with organomagensium compounds is an effective method of synthesizing iso trans alkenes with a centrally located double bond.

3. The reaction of 1,4-dipropenyl dichloride with methylmagnesium bromide produced 2,5-dimethyl-3-hexene (trans form) with 20% of the theoretical yield.

4. The reaction of 1,4-dipropenyl dichloride with ethylmagnesium bromide produced 3,6-dimethyl-4-octene (trans form) with 25% of the theoretical yield.

5. The synthesized hydrocarbons were identified by their constants, by analysis, by a study of their oxidation and bromination products, and by examination of their combined light-scattering spectra.

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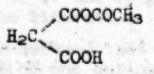
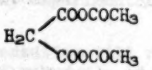
# RESEARCH ON β-LACTONES AND β-LACTONIC ACIDS

## VI. THE MECHANISM OF THE FORMATION OF β-LACTONIC ACIDS

N. S. Wulfson

In our previous report [1] we demonstrated that the reaction of malonic acid with acetic anhydride yields two mixed anhydrides – one acid (I) and the other neutral (II):


(I)


(II)

Ott's paper [2] has shown that these mixed anhydrides (the so-called "Ott reagent"), condensed with acetone, yield a β-lactone that is isopropylidenemalonic acid (III). The "Ott reagent" contains concentrated sulfuric acid, which catalyzes the formation of the mixed anhydrides. It was important to ascertain whether it acts similarly during the condensation with acetone. Experiment 2, however, shows that sulfuric acid does not affect this latter reaction, inasmuch as a β-lactonic acid similar to (III) is also synthesized even when mixed anhydrides prepared without the use of sulfuric acid (the so-called "primary mixed anhydrides"; cf [1]) are condensed with acetone.

Employment of this reaction with a number of carbonyl compounds, such as benzaldehyde (Experiment 6), m-nitrobenzaldehyde (Experiment 8), and others, demonstrated the universal nature of this reaction, which is a modification of the Meldrum-Ott synthesis [2,3].

Inasmuch as the "Ott reagent" and the "primary mixed anhydride" constitute mixtures of two mixed anhydrides – the acid (I) and the neutral (II), we had to determine which of the two yields a β-lactonic acid when reacted with acetone. This was all the more interesting inasmuch as we know that a mixed anhydride of monomethyl malonate and acetic acid is unable to produce the corresponding ester of a β-lactonic acid when condensed with acetone. A solution to this problem could be found only if we were able to synthesize each of the mixed anhydrides (I) and (II) separately. As has been pointed out already, this can be done by reacting acetyl chloride with the acid or neutral silver salt of malonic acid [1]. Reacting neutral silver malonate with acetyl chloride in the presence of anhydrous acetone yielded a β-lactonic acid that was identical with that synthesized previously (Experiment 4). No such reaction took place when the acid silver malonate was used. Hence, only the neutral mixed anhydride (II) can be condensed with acetone.

The synthesis of a β-lactonic acid from silver malonate and acetyl chloride is a new method of synthesizing such compounds. We had to determine, first, whether this reaction holds good for other carbonyl compounds besides acetone, and, second, whether it takes place only with a mixed anhydride containing the acetyl radical, or with other mixed anhydrides as well.

The reaction of neutral silver malonate with acetyl chloride in the presence

of cyclohexanone (Experiment 9) and of benzaldehyde (Experiment 7) yielded the corresponding β-lactonic acids and proved the universal applicability of this reaction.

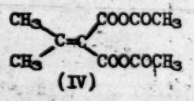
Substitution of benzoyl chloride for acetyl chloride in the reaction, carried out in the presence of acetone, enabled us to prove that this reaction results in the formation of β-lactonic acids with other mixed anhydrides as well. To be sure, this substitution has no preparative significance, inasmuch as the isolation of the resulting β-lactonic acids from the benzoic acid simultaneously formed is extremely difficult.

The general equation for the reaction, say, for condensation with acetone, may be expressed as follows:

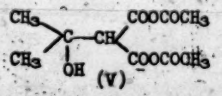
(II) (III)

This equation gives no inkling, however, of the nature of the intermediate stages involved or of the by-products, nor is there any experimental material on this point in the literature.

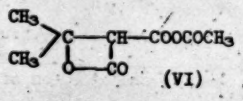
It may be assumed that the first stage of condensation will result in the formation of one of the following products: 1) a mixed anhydride of isopropylidenemalonic and acetic acids (IV); 2) a neutral mixed anhydride of β-hydroxyisopropylmalonic and acetic acids (V); or, lastly, 3) the mixed anhydride of the β-lactone of isopropylidenemalonic and acetic acids (VI) directly:



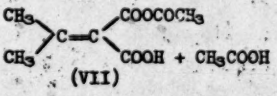
(IV)



(V)



(VI)



(VII)

The subsequent conversion of these compounds into the β-lactonic acid (III) may be imagined as follows:

1) The mixed anhydride of isopropylidenemalonic and acetic acids (IV), partially saponified by atmospheric moisture, yields the acid mixed anhydride of isopropylidenemalonic and acetic acids (VII); but then it is hard to understand why the mixed acid malonic-acetic anhydride, which is converted tautomerically into the mixed anhydride of the β-lactone of isopropylidenemalonic and acetic acids (VI), does not condense with acetone directly. Anhydride (VI), when saponified by atmospheric moisture, yields the β-lactone of isopropylidenemalonic acid (III) directly.

2) The mixed anhydride of β-hydroxyisopropylmalonic and acetic acids (V) is transformed by an intramolecular process into the mixed anhydride of the β-lactone of isopropylidenemalonic and acetic acids (VI), which is converted by atmospheric moisture, as in Case 1, into the β-lactone of isopropylidenemalonic acid (III).

3) The transformation of the mixed anhydride (VI) into the β-lactonic acid (III) has been discussed above.

It is possible to check the correctness of Supposition 1 experimentally by

preparing the corresponding mixed anhydride of isopropylidene malonic and acetic acids (IV) and investigating its transformations in the condensation of the "Ott reagent" or of the primary mixed anhydride with acetone, which results, as we know, in the formation of the β-lactone of isopropylidenemalonic acid (III).

The addition of 1 drop of concentrated sulfuric acid to a mixture of isopropylidenemalonic acid and acetic anhydride causes complete dissolution. But after standing for a long time, followed by the driving off of the acetic anhydride in vacuum, the initial isopropylidenemalonic acid is recovered unchanged (Experiment 10). When acetyl chloride is reacted with neutral silver isopropylidenemalonate or benzalmalonate in anhydrous acetone (Experiments 11 and 12), the reaction is very violent, but we recovered the initial isopropylidene- and benzalmalonic acids instead of the expected β-lactonic acids.

A similar series of tests (the action of acetic anhydride upon the acid, and the action of acetyl chloride upon the silver salt) was run with isopropylidene-acetic acid in the hope of obtaining the corresponding β-lactone. These experiments were likewise fruitless. We recovered either isopropylidene-acetic acid or its symmetrical anhydride (Experiments 13 and 14).

Hence, it may be considered experimentally proved that Supposition 1 regarding the mechanism of formation of β-lactonic acids is false.

If supposition 2 or 3 were correct, it might be expected that the reaction of alcohol with the crude condensation product would yield the corresponding esters: an ester of the β-lactonic acid (III) or the hydroxy ester of the dicarboxylic acid (V). But in the latter case, we would also have to expect such β-hydroxy compounds to be extremely unstable, easily decomposing into the initial carbonyl compounds and malonic ester.

We first ascertained that complete condensation of acetone with the mixed anhydride requires a long time. The filtrate resulting from the reaction of acetyl chloride with the silver malonate was divided into two equal parts. One part was given two more hours of treatment, and the initial malonic acid was recovered. The other part, left standing overnight, yielded a β-lactonic acid (III), that was identical with that previously prepared (Experiment 15).

To explore the reaction between alcohol and the condensation products, all the operations were carried out under conditions that precluded the entrance of atmospheric moisture, and the reaction product was sealed in a carefully desiccated ampoule. One day later, the reaction product was poured into absolute methanol. This yielded acetic acid (identified as its p-nitrobenzyl ester) and dimethyl malonate. A small quantity of the reaction product quickly crystallized as long needles, which proved to be the β-lactonic acid (III), when allowed to stand in air. This indicates that condensation took place and that the formation of the dimethyl malonate was the result of a secondary process of decomposition of the condensation product, in accordance with the supposition expressed previously.

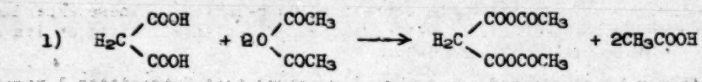
Because of our fear that the methyl ester of the β-lactonic acid (III) might prove to be a liquid, and its isolation in the pure state might result in decomposition of the molecule, we tried to carry out the reaction in such a way as to recover crystalline products. To accomplish this, phenol was substituted for the methanol, but, here again, only the diphenyl malonate was recovered (Experiment 17). Hence, it may be considered proven that the first stage of condensation of the mixed malonic-acetic anhydride with acetone is the mixed anhydride of β-hydroxyisopropylmalonic and acetic acids.

The fact that we were unable to isolate a β-lactonate not only disproves supposition 3 concerning the mechanism of the condensation reaction, but also casts

doubt upon the correctness of the assumed mechanism of the subsequent transformations of the mixed anhydride of β-hydroxyisopropylmalonic and acetic acids (V) into the β-lactonic acid (III), inasmuch as the next stage is the formation of the mixed anhydride of the β-lactone of isopropylidenemalonic and acetic acids (VI).

Study of the by-products of the reaction, together with an experiment run to determine whether atmospheric moisture is required for these processes (the latter may serve merely as a supplementary, but not as a primary proof, inasmuch as it is extremely difficult to ensure the absolute exclusion of atmospheric moisture), would be of great importance in resolving the problem of the subsequent transformations of the anhydride (V).

The tests we ran (Experiment 18) proved that the second product of the condensation of the mixed malonic-acetic anhydride with acetone is acetic anhydride, and that atmospheric moisture plays no part in this reaction. The foregoing makes it possible to represent the mechanism of the formation of the β-lactone that corresponds to isopropylidenemalonic acid (III) as follows:



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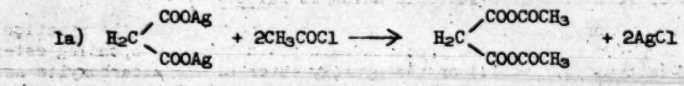
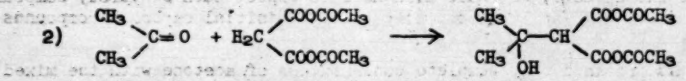
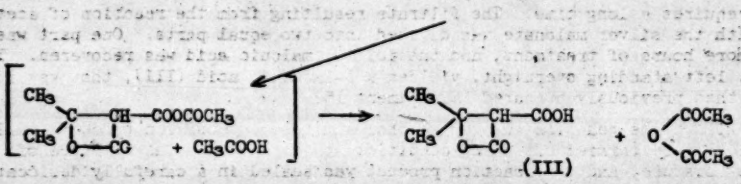




(V)



(III)

In conclusion, I must express my heartfelt gratitude to Academician V.M. Rodionov and Prof. M.M.Shemyakin for their extremely valuable counsel and instructions.

## EXPERIMENTAL

Condensation with acetone.1. 12 g of acetone is added to the "Ott reagent" prepared with 10 g of malonic acid (cf Report V, Experiment 1) [1]; this causes considerable heating, and the reaction mass turns brown. The reaction mass crystallizes overnight. Recrystallization from acetone or benzene yields 8 g of white, acicular crystals with a m.p. of 96-97°. The yield of the β-lactone of isopropylidenemalonic acid is 55.5% of the theoretical.

Titration: 0.781 g substance; 10 ml 70% alcohol.

| | | |
|---|---|---|
| | Consumed: 0.1N NaOH in the cold ..... | 5.34 ml. |
| | Consumed: after boiling for two hours with excess alkali ... | 10.75 ml. |
| $C_6H_8O_4$. | Computed: for neutralization ..... | 5.43 ml. |
| | Computed: for neutralization and saponification ..... | 10.86 ml. |

Acidulation did not result in recovery of the initial lactonic acid.

Analysis of the silver salt, prepared by precipitation of a lactonic acid solution, neutralized with alkali in the cold, with silver nitrate:

Found %: Ag 43.10.
$C_6H_7O_4Ag$. Calculated %: Ag 43.00.

Analysis of the silver salt, prepared by precipitation of a lactonic acid solution, neutralized after boiling with alkali, with silver nitrate:

Found %: Ag 60.09.
$C_6H_6O_4Ag_2$. Calculated % Ag 60.31.

2. 12 g of acetone is added to the "primary mixed anhydride," prepared with 10 g of malonic acid (cf. Report V, Experiment 3) [1]; further treatment is as outlined above. This yields 7 g (48.6% of the theoretical) of white acicular crystals with a m.p. of 96-97°. A test sample mixed with the end product of Experiment 1 fuses at 96-97°.

Titration: 0.0913 g substance: 10 ml 70% alcohol.

| | | |
|---|---|---|
| | Consumed: 0.1 N NaOH in the cold | 6.39 ml. |
| | Consumed: after boiling for 2 hours with excess alkali | 12.72 ml. |
| $C_6H_8O_4$. | Computed: for neutralization | 6.33 ml. |
| | Computed: for neutralization and saponification | 12.66 ml. |

3. 12 g of acetone is added to the "primary mixed anhydride," prepared with 10 g of malonic acid by heating (cf Report V, Experiment 4) [1]; further treatment is as outlined above. This yields 5 g of white acicular crystals with a m.p. of 96-97°. A test sample mixed with the preparation described above exhibits no depression.

Titration: 0.0626 g substance; 10 ml 70% alcohol.

| | | |
|---|---|---|
| | Consumed: 0.1N NaOH in the cold | 4.31 ml. |
| | Consumed: after boiling for 2 hours with excess alkali | 8.70 ml. |
| $C_6H_8O_4$. | Computed: for neutralization | 4.31 ml. |
| | Computed: for neutralization and saponification | 8.62 ml. |

4. 6.4 g of neutral silver malonate is placed in 10 g of absolute acetone, and 10 g of acetyl chloride is added drop by drop with constant stirring. The solution heats up considerably and turns yellow. After cooling, the precipitate of silver chloride is filtered out and washed with acetone, and the combined acetone mother liquor is set aside to stand overnight. Then the solvent is driven off in a slight vacuum, and the residue is recrystallized from acetone or benzene. This yields 1.4 g (48.6% of the theoretical) of a white crystalline substance with a m.p. of 95-96°. A test sample mixed with the preparations described above exhibits no depression.

Titration: 0.0386 g substance: 10 ml 70% alcohol.

| | | |
|---|---|---|
| | Consumed: 0.1N NaOH in the cold | 2.8 ml. |
| | Consumed: after boiling for 2 hours with excess alkali | 5.23 ml. |
| $C_6H_8O_4$. | Computed: for neutralization | 2.68 ml. |
| | Computed: for neutralization and saponification | 5.36 ml. |

5. 6.4 g of neutral silver malonate is placed in 10 ml of absolute acetone, and 5.65 ml of benzoyl chloride is added drop by drop with constant stirring. The subsequent treatment is the same as in the preceding experiment. Repeated fractional recrystallization from benzene and from petroleum ether yields two fractions: one with a m.p. of 96-97°, does not exhibit any depression when mixed with a sample

of the β-lactone of isopropylidenemalonic acid.

Titration: 0.0265 g substance; 10 ml 70% alcohol.

| | | |
|---|---|---|
| | Consumed: 0.1N NaOH in the cold | 1.9 ml. |
| | Consumed: after boiling for 2 hours with excess alkali | 8.7 ml. |
| $C_6H_8O_4$. | Computed: for neutralization | 1.8 ml. |
| | Computed: for neutralization and saponification | 3.6 ml. |

The second fraction fuses at 119-119.5° and exhibits no depression in a mixed test sample with benzoic acid.

Titration: 0.0814 g substance: 10 ml 50% alcohol.

| | | |
|---|---|---|
| | Consumed: 0.1N NaOH | 6.75 ml. |
| $C_7H_8O_2$. | Computed: for neutralization | 6.67 ml. |

Condensation with benzaldehyde. 6. 10 g of benzaldehyde is added to the "primary mixed anhydride," prepared with 10 g of malonic acid; this results in very intense heating of the mixture. Subsequent treatment is the same as in Experiment 1. This yields 5 g (27.9% of the theoretical) of white, acicular crystals that fuse with decomposition at 145-146° (from a mixture of acetone and benzene).

Titration: 0.0343 g substance: 10 ml 70% alcohol.

| | | |
|---|---|---|
| | Consumed: 0.1N NaOH in the cold | 1.79 ml. |
| | Consumed: after boiling for 15 minutes with excess alkali | 3.69 ml. |
| $C_{10}H_8O_4$. | Computed: for neutralization | 1.78 ml. |
| | Computed: for neutralization and saponification | 3.57 ml. |

Acidulation did not result in recovery of the initial lactonic acid.

Analysis of the silver salt, prepared by precipitating a lactonic acid solution, neutralized with alkali in the cold, with silver nitrate:

Found %: Ag 36.40.

$C_{10}H_7O_4Ag$. Calculated %: Ag 36.43.

Analysis of the silver salt, prepared by precipitating the lactonic acid solution, neutralized with alkali after boiling, with silver nitrate:

Found %: Ag 53.20.

$C_{10}H_6O_4Ag_2$. Calculated %: Ag 53.18.

7. 6.4 g of neutral silver malonate is added to 10 g of benzaldehyde, and 5 g of acetyl chloride is added drop by drop with constant stirring; this results in intense heating. Subsequent treatment is the same as in Experiment 4. This yields 1 g of a crystalline substance with a m.p. of 145-146° (from a mixture (1:1) of acetone and benzene). A test sample mixed with the β-lactone of benzalmalonic acid (Experiment 6) exhibits no depression.

Titration: 0.0425 g substance: 10 ml 70% alcohol.

| | | |
|---|---|---|
| | Consumed: 0.1N NaOH in the cold | 2.27 ml. |
| | Consumed: after boiling 15 minutes with excess alkali | 4.52 ml. |
| $C_{10}H_8O_4$. | Computed: for neutralization | 2.21 ml. |
| | Computed: for neutralization and saponification | 4.42 ml. |

Condensation with m-nitrobenzaldehyde. 8. 15 g of m-nitrobenzaldehyde is added to the "Ott reagent" (or to the primary mixed anhydride), prepared with 10 g of malonic acid, and the whole is gently heated until dissolution is complete. The viscous orange mass is set aside to stand overnight. Decantation with ether yields a small quantity of white crystals (0.4 g) with a m.p. of 133-134.5° (from a mixture of acetone and chloroform), which exhibit no depression when mixed in a test sample with malonic acid. The ether solution is treated with soda. The soda layer

is acidulated with 10% sulfuric acid and extracted with ether; the ether extract is washed with water, dried, and decolorized with activated charcoal; and the ether is driven off. This yields a thick oil that does not crystallize for a long time. The m.p. is 158.5-159° after recrystallization from methanol.

Titration: 0.1854 g substance:

| | | |
|---|---|---|
| | Consumed: 0.1N NaOH in the cold | 7.9 ml. |
| | Consumed: after boiling for 1 hour with excess alkali | 15.8 ml. |
| $C_{10}H_7O_6N$. | Computed: for neutralization | 7.82 ml. |
| | Computed: for neutralization and saponification | 15.64 ml. |

Acidulation did not result in recovery of the initial lactonic acid.

Analysis of the silver salt, prepared by precipitating a lactonic acid solution, neutralized in the cold, with silver nitrate:

Found %: Ag 31.09.
$C_{10}H_8O_6NAg$. Calculated %: Ag 31.39.

Analysis of the silver salt, prepared by precipitating a lactonic acid solution, neutralized after boiling with alkali, with silver nitrate:

Found %: Ag 47.96.
$C_{10}H_5O_6NAg_2$. Calculated %: Ag 47.89.

Analysis of the lactonic acid for nitrogen: (Dumas).

Found %: N 6.14.
$C_{10}H_7O_6N$. Calculated %: N 5.91.

Condensation with cyclohexanone. 9. 6.4 g of neutral silver malonate is added to 10 g of cyclohexane, and 6 g of acetyl chloride is added drop by drop with constant stirring. Further treatment is the same as that described in Experiment 4. This yields 1.5 g of a white crystalline substance with a m.p. of 84.85°. A test sample mixed with the β-lactone of cyclohexylidenemalonic acid prepared by a different method exhibits no depression.

Titration: 0.1546 g substance:

| | | |
|---|---|---|
| | Consumed: 0.1 NaOH in the cold | 8.26 ml. |
| | Consumed: after boiling for 1 hour with excess alkali | 16.78 ml. |
| $C_9H_{12}O_4$. | Computed: for neutralization | 8.4 ml. |
| | Computed: for neutralization and saponification | 16.81 ml. |

Analysis of the silver salt, prepared by precipitation of a lactonic acid solution, neutralized in the cold, with silver nitrate:

Found %: Ag 37.16.
$C_9H_{11}O_4Ag$, Calculated %: Ag 37.11.

Analysis of the silver salt, prepared by precipitation of a lactonic acid solution, neutralized after boiling with alkali, with silver nitrate:

Found %: Ag 54.37.
$C_9H_{10}O_4Ag_2$. Calculated %: Ag 54.27.

Endeavor to lactonate isopropylidenemalonic acid. 10. One drop of concentrated sulfuric acid is added to a mixture of 0.3 g of isopropylidenemalonic acid and 2 g of acetic anhydride, resulting in complete dissolution. The solution is set aside for three days, after which it is poured into water and extracted with ether. The extract is dessicated, and the ether driven off. This yields 0.25 g of a white crystalline substance with a m.p. of 166-168° (from a mixture of acetone and chloroform). A test sample mixed with the initial isopropylidenemalonic acid exhibits no depression.

11. 1.4 g of silver isopropylidenemalonate is added to 10 ml of absolute acetone, and 5 g of acetyl chloride is added drop by drop with constant stirring. Subsequent treatment is the same as in Experiment 4. This yields 0.3 g of a white crystaline substance with a m.p. of 164-166° (from an acetone-chloroform mixture), which exhibits no depression when mixed in a test sample with the initial isopropylidenemalonic acid.

Endeavor to lactonate benzalmalonic acid. 12. 4 g of silver benzalmalonate is added to 10 ml of absolute acetone, and 4 g of acetyl chloride is added with constant stirring. Subsequent treatment is the same as in Experiment 4. This yields 1.8 g of a white crystalline substance with a m.p. of 193-194° (from 60% alcohol), which exhibits no depression when mixed in a test sample with the initial benzalmalonic acid.

Endeavor to lactonate isopropylideneacetic acid. 13. 3 drops of concentrated sulfuric acid are added to a mixture of 6.2 g of isopropylideneacetic acid and 25 ml of acetic anhydride, resulting in complete dissolution, noticeable chilling, and the solution turning yellow. It is heated to 60° for 2 hours over a water bath and then is set aside for 2 days. The excess acetic anhydride is driven off in vacuum. The residue is dissolved in ether and extracted with a soda solution. The ether solution is washed with water and desiccated, and the ether is driven off. The residue is distilled in vacuum. B.p. 140-142° at 13 mm or 117-118° at 2 mm. The yield of the anhydride of isopropylideneacetic acid is 4 g.

Saponification: 0.1100 g substance: alkali used: 12.3 ml.
$C_{10}H_{14}O_3$. Calculated: 12.1 ml.
Found %: C 65.52; H 7.94.
$C_{10}H_{14}O_3$. Calculated %: C 65.91; H 7.74.

When treated with an aqueous aniline solution, it yields an anilide, white acicular crystals with a m.p. of 127.5-128° (from alcohol).

The soda solution is acidulated with 10% sulfuric acid and extracted with ether, the extract is washed with water and desiccated, and the ether is driven off. This yields 0.5 g of a crystalline substance with a m.p. of 66-68° (from water), which exhibits no depression when mixed in a test sample with the initial isopropylideneacetic acid.

14. 3 g of silver isopropylideneacetate is added to 20 ml of absolute ether, and 1.13 g of acetyl chloride is added drop by drop with constant stirring. The subsequent treatment is the same as in Experiment 4. This yields 1 g of white acicular crystals with a m.p. of 67.5-69° (from water), which exhibit no depression when mixed in a test sample with isopropylideneacetic acid.

Research on the mechanism of the condensation reaction. 15. 6.4 g of neutral silver malonate is added to 15 ml of absolute acetone, and 10 g of acetyl chloride is added drop by drop with constant stirring. Subsequent treatment is the same as in experiment 4. After the silver chloride is removed, the filtrate is separated into two parts: one part is treated two hours later, and the other the next day. The first part yields a crystalline substance with a m.p. of 134-135° (from an acetone-chloroform mixture), which exhibits no depression in a mixed test sample with malonic acid; the second part yields acicular crystals with a m.p. of 95-96° (from acetone or benzene), which exhibit no depression when mixed in a test sample with the β-lactone of isopropylidenemalonic acid.

Titration: 0.0386 g substance:
Consumed: 0.1N NaOH in the cold .....2.8 ml.
Consumed: after boiling for 1 hour with excess alkali ..5.23 ml.
$C_6H_8O_4$. Computed: for neutralization..... 2.68 ml.
Computed: for neutralization and saponification ..... 5.36 ml.

16. 25.6 g of neutral silver malonate and 80 ml of absolute acetone are poured into a flask connected to a tower containing $P_2O_5$, and 60 g of acetyl chloride is added drop by drop with constant stirring. After the silver chloride has been removed, the filtrate is sealed into an ampoule and left to stand overnight. Then the contents of the ampoule are carefully poured into 200 ml of absolute methanol (a few milliliters are left to stand exposed to the air). First, the excess acetone, methanol, and methyl acetate are driven off at standard pressure and 55-72°. Then 20-30° and 77-80° fractions are collected at 15-mm vacuum. The first fraction boils 90-100° at standard pressure, smells like acetic acid, and yields a p-nitrobenzyl ester with a m.p. of 77.5-78° (from alcohol), which exhibits no depression when mixed in a test sample with p-nitrobenzyl acetate. The second fraction boils at 179-182° at standard pressure, and has a $n_D^{20}$ 1.4140, which corresponds to the data for dimethyl malonate. The liquid left to stand exposed to the air after the ampoule was opened crystallized rapidly into long needles. M.p. 93-94°. A test sample mixed with the β-lactone of isopropylidenemalonic acid exhibits no depression.

17. The preceding experiment is repeated with 15.2 g of phenol taking the place of the methanol. This yields dipheryl malonate, with a m.p. of 48.5-49.5°, which exhibits no depression when mixed with an analytical test sample.

18. 6.4 g of neutral silver malonate is added to 10 ml of absolute acetone and treated with 3.1 g of acetyl chloride (somewhat less than theoretically required). The subsequent treatment is the same as in Experiment 4. The contents of the ampoule are emptied into a Claisen flask, and the excess acetone is driven off in a slight vacuum at a temperature that does not exceed 35-40°. Then the residue is evaporated to dryness at 5 mm and 40-45°. This yields 0.5 g of a colorless liquid with the acrid odor of acetic anhydride. The silver-nitrate test for halogens is negative (no acetyl chloride is present). Agitation with an aqueous solution of aniline yields a white precipitate with a m.p. of 112-113°. A test sample mixed with acetanilide exhibits no depression. The residue left in the flask consists of brown acicular needles that fuse at 93-94.5° after recrystallization from benzene and exhibit no depression in a test sample mixed with the β-lactone of isopropylidenemalonic acid.

## SUMMARY

1. It has been established that only the neutral mixed malonic-acetic anhydride condenses with carbonyl compounds, forming β-lactonic acids. The acid mixed malonic-acetic anhydride does not react.

2. It has been shown that sulfuric acid, which catalyzes the formation of malonic-acetic anhydrides, does not participate in the ensuing condensation with carbonyl compounds. This has made it possible to make some modifications in the method of synthesizing β-lactonic acids described in the literature and to evolve a new method, consisting of the reaction of neutral silver malonate with acetyl chloride in the presence of the carbonyl compound.

3. It has been established that the initial stage of the condensation of the mixed malonic-acetic anhydride with acetone is a mixed anhydride of β-hydroxyisopropylmalonic and acetic acids, which reacts intramolecularly, being transformed into the β-lactone of isopropylidenemalonic acid by the acetic acid that is formed.

## LITERATURE CITED

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*See CB translation, pp. 1369 ff.

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# RESEARCH ON β-LACTONES AND β-LACTONIC ACIDS

## VII. THE RELATIONSHIP BETWEEN THE STRUCTURE OF A CARBONYL COMPOUND AND ITS CONDENSATION PRODUCT WITH MALONIC ACID

N. S. Wulfson

In my previous reports [1,2] I considered in detail the mechanism of the formation of β-lactonic acids that are derivatives of malonic acid. This research was done on condensations with acetone. Moreover, this reaction was also applied to some other carbonyl compounds, such as, benzaldehyde [2,3,4], m-nitrobenzaldehyde, cyclohexanone [2], etc. The very first experiments demonstrated, however, that not all aldehydes and ketones behave the same way in the condensation conditions under investigation. Whereas some of them, such as those listed above, give rise to β-lactonic acids, others react with a mixed malonic-acetic anhydride to form acid esters of malonic acid or do not react at all. This led me to undertake a study of the relationship between the structure of the initial carbonyl compound and its condensation product with a mixed malonic-acetic anhydride. This research proved that no β-lactonic acids are formed in the following cases:

1) When the carbonyl compound contains a hydroxyl group in addition to an aldehyde or ketone group, (such as, diacetone alcohol), malonates are formed;

2) When the carbonyl compound is highly susceptible to autocondensation (aldolization), resulting in the formation of a hydroxyl group (acetaldehyde or propionic aldehyde, for instance), malonates again being formed;

3) When the carbonyl compound exists in the enol form or when the condensation conditions favor enolization (as in acetoacetic ester, mesityl oxide, pseudoionone, and benzalacetone), enol malonates being formed;

4) When the carbonyl compound has a marked tendency to form diacetates (as in chloral).

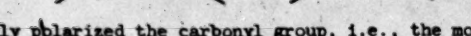
Wagscheider and Spath [5] point out that concentrated sulfuric acid catalyzes the formation of diacetates. It might have been expected that in some instances it would be possible to obtain the corresponding β-lactonic acid instead of the aldehyde diacetate in the Ott reaction as modified by the present author [2]. This has been confirmed for cinnamic aldehyde. Lastly:

5) When the carbonyl compound undergoes a farreaching change in the condensation reaction (such as complete tarring), as occurs with furfural.

Everything set forth above refers to carbonyl compounds that contain some form or other of hydroxyl group. This does not mean that all other carbonyl compounds tend to form β-lactonic acids. This problem involves the reactivity of the carbonyl group.

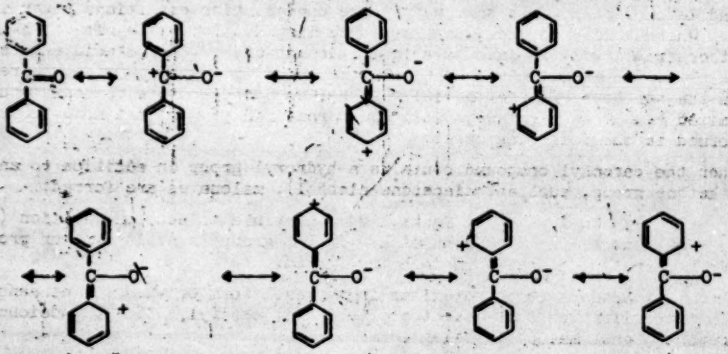
The formation of a mixed anhydride of β-hydroxyisopropylmalonic and acetic acids, which is the first stage of the formation of β-lactonic acids [2], must be looked upon as a reaction of the carbonyl group with the methylene component of the mixed anhydride:

The more highly polarized the carbonyl group, i.e., the more prominent the resonance structure (B):

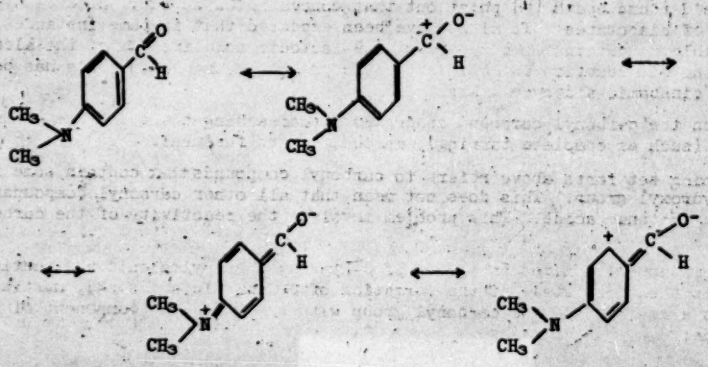


is within it, the easier it will be for such a reaction to take place, inasmuch as this type of structure facilitates the addition of both the organic anion of the methylene component and the hydrogen ion.

Resonance structures of this sort occur chiefly in aliphatic and alicyclic ketones; this explains the ease with which β-lactonic acids are formed in condensations with acetone, cyclohexanone, menthone, etc. Whenever resonance structures in which the positive charge is not on the carbon atom of the carbonyl group are present in large quantities, the greater the proportion of these structures, the harder it will be to effect condensation, inasmuch as the addition of the organic anion of the methylene group to the carbonyl group's carbon is hampered. Benzophenone, for example, which consists of a superposition of the following resonance structures:



and p-dimethylaminobenzaldehyde:



do not react with mixed malonic-acetic anhydride.

Though benzaldehyde and some of its derivatives (m-nitro- and o-, m-, and p-chlorobenzaldehydes) as well as acetophenone possess resonance structures that lack the positive charge on the carbon atom of the carbonyl group, the proportion of these structures is not very high, apparently, inasmuch as these compounds yield the corresponding β-lactonic acids when condensed with mixed malonic-acetic anhydride.

We list below some selected condensations with various carbonyl compounds that bear out the foregoing assertions.

1. Condensation with acetone, yielding the β-lactone of isopropylidenemalonic acid, discussed in detail both in the literature as well as in my previous reports [1,2,3].

2. Condensation with acetophenone yields the β-lactone of β-phenylethylidenemalonic acid as white acicular crystals with a m.p. of 91.5-92°.

3. Condensation with cyclohexanone yields the β-lactone of cyclohexylidenemalonic acid, described in the literature and in my previous report [2].

4. Condensation with methone yields the β-lactone of methylidenemalonic acid, as white acicular crystals with a m.p. of 107.5-108° (with partial decomposition).

5. Condensation with hydrocinnamic aldehyde produces a slight yield of the β-lactone of hydrocinnamalmalonic acid, as a white crystalline substance with a m.p. of 139-140°.

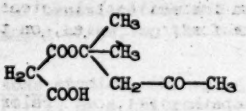
6. Condensation with benzaldehyde, described in detail in the literature and in my previous reports [2,3], yields the β-lactone of benzalmalonic acid.

7. Condensation with m-nitrobenzaldehyde, resulting in the formation of the β-lactone of m-nitrobenzalmalonic acid, described in my previous report [2].

8. Condensation with ortho, meta, and para nitrobenzaldehydes results in the formation of β-lactones of the corresponding nitrobenzalmalonic acids

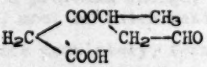
9. Condensation with cinnamic aldehyde, which will be discussed in detail in my next report, results in the formation of the β-lactone of cinnamalmalonic acid.

10. Condensation with diacetone alcohol results in the formation of a noncrystallizing oily substance, to which the structure of an acid ester of malonic acid:



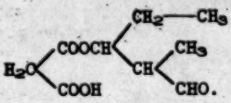
has been attributed on the basis of its own titration data and that of its semicarbazone (m.p. 232-234°), as well as of the determination of nitrogen in the latter.

11. Condensation with acetaldehyde results in the formation of a noncrystallizing oil that decomposes when heated. This substance has been given the structure of an acid ester of acetaldol and malonic acid:

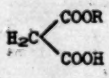


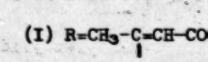
on the basis of its own titration data and that of its semicarbazone (m.p. 152-154°), as well as of the determination of nitrogen in the latter.

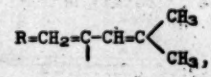
12. Condensation with propionic aldehyde is similar to that with acetaldehyde, yielding an acid ester of propaldol and malonic acid (semicarbazone with a m.p. of 177-179°):

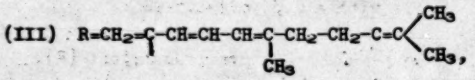


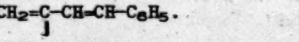
13. Condensation with acetoacetic ester yields a yellow oily substance. The structure of an acid ester of the enolic form of acetoacetic ester and malonic acid (I):



(I) 

(II) 

(III) 

(IV) 

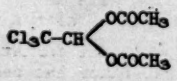
has been attributed to this substance on the basis of titration data, analysis of the silver salt, and analysis of the p-nitrobenzyl ester (m.p. 202.5-204°).

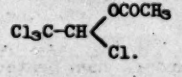
14. Condensation with mesityl oxide yields a viscous yellow oil with an acrid odor, which decomposes when heated. The structure of an acid ester of the enolic form of mesityl oxide and malonic acid (II) has been attributed to this substance, by analogy with the preparations described above, from the titration data and analysis of the silver salt.

15. Condensation with pseudoionone yields an extremely viscous, noncrystallizing, orange-colored oil with an odor resembling that of pseudoionone, which decomposes when heated. The structure of an acid ester of the enolic form of pseudoionone and malonic acid (III) has been ascribed to it, as in the preceding case, on the basis of titration data and the analysis of the silver salt.

16. Condensation with benzaldehyde yields a viscous, noncrystallizing, yellowish-orange oil, which decomposes when heated, even in vacuum. The structure of an acid ester of the enolic form of benzalacetone and malonic acid (IV) has been ascribed to it, as in the foregoing cases, on the basis of titration data and the analysis of its silver salt.

17. Under the reaction conditions studied, chloral gives rise to a diacetate, described by Wegscheider and Spath [5,9], or a chloroacetate, described by Meyer and Dilk [10]:





18. Citral undergoes a profound change, resulting in the formation of a small quantity of p-cymene, most of which resinifies.

19. Furfural resinifies completely, forming a black resinous mass.

20. p-Dimethylaminobenzaldehyde and benzophenone remain unchanged.

In conclusion, the author wishes to express his deep appreciation of the valuable counsel and instructions given him by Academician V.M.Rodionov and Prof. M.M. Shemyakin.

## EXPERIMENTAL

1. Condensation with acetophenone. 10 g of acetophenone is added to the "Ott reagent," prepared with 10 g of malonic acid (cf Report V [1], Experiment 1), and the mixture is set aside for 48 hours. The dark brown reaction mass is poured into water and extracted with ether; the ether extract is washed with water and desiccated and the ether is driven off. The residue is recrystallized from a benzene-gasoline mixture, yielding 2.5 g of white acicular crystals with a m.p. of 91.5-92°.

Titration: 0.0292 g substance; 10 ml 70% alcohol.

| | | |
|---|---|---|
| | Consumed. 0.1N NaOH in the cold ..... | 1.46 ml. |
| | Consumed: after boiling for 15 minutes with alkali ..... | 2.84 ml. |
| $C_{11}H_{10}O_4$. | Computed: for neutralization ..... | 1.41 ml. |
| | Computed: for neutralization and saponification ..... | 2.83 ml. |

Found %: C 64.14; H 5.18.
$C_{11}H_{10}O_4$. Calculated %: C 64.07; H 4.85.
Found %: Ag 34.64, 34.22.
$C_{11}H_9O_4Ag$. Calculated %: Ag 34.50.

When a solution of the lactonic acid that has been thoroughly boiled with alkali is acidulated, the initial lactonic acid is recovered.

2. Condensation with menthone. 15 g of menthone is poured into an "Ott reagent," prepared with 10 g of malonic acid, and the mixture is set aside for one day. The viscous brown mass is then dissolved in ether and treated with a soda solution. 8 g of unreacted menthone is recovered from the ether layer. The soda solution is acidulated with 10% sulfuric acid and extracted with ether; the ether solution is washed with water, dried, and decolorized with activated charcoal; and the ether is driven off. The residue is recrystallized from chloroform, benzene, or methanol. This yields 4.8 g of the β-lactone of menthylmalonic acid as white acicular crystals with a m.p. of 107.6-108° (with decomposition).

Titration: 0.0858 g substance:

| | | |
|---|---|---|
| | Consumed: 0.1N NaOH in the cold ..... | 3.6 ml. |
| | Consumed: after boiling for 1 hour with alkali ..... | 7.2 ml. |
| $C_{13}H_{20}O_4$. | Computed: for neutralization ..... | 3.58 ml. |
| | Computed: for neutralization and saponification ..... | 7.15 ml. |

Acidulation resulted in precipitation of the initial lactonic acid.

Analysis of the silver salt precipitated from a solution of the lactonic acid, neutralized in the cold with alkali, by silver nitrate:

Found %: Ag 31.21.
$C_{13}H_{18}O_4Ag$. Calculated %: Ag 31.12.

Analysis of the silver salt precipitated from a solution of the lactonic acid, neutralized by boiling with alkali, by silver nitrate:

Found %: Ag 47.90.
$C_{13}H_{16}O_4Ag_2$. Calculated %: Ag 47.58.

Analysis of the lactonic Acid:

Found %: C 65.25; H 8.29.
$C_{13}H_{20}O_4$. Calculated %: C 65.00; H 8.33.

3. Condensation with hydrocinnamic aldehyde. 13.5 g of hydrocinnamic aldehyde is poured into an "Ott reagent," prepared with 10 g of malonic acid, and then is treated as described in Experiment 2. Recrystallization from an acetone-methanol

mixture yields 3.5 g of the β-lactone of hydrocinnamalmalonic acid as white crystal-substance with a m.p. of 139-140°.

| | | |
|---|---|---|
| | Titration: 0.0510 g substance: | |
| | Consumed: 0.1N NaOH in the cold ..... | 2.3 ml. |
| | Consumed: after boiling for 1 hour with alkali ..... | 4.6 ml. |
| $C_{12}H_{12}O_4$. | Computed: for neutralization ..... | 2.32 ml. |
| | Computed: for neutralization and saponification ..... | 4.64 ml. |

The initial lactonic acid is not recovered after acidulation.

Analysis of the silver salt precipitated from a solution of the lactonic acid, neutralized with alkali in the cold, by silver nitrate:

Found %: Ag 32.99.

$C_{12}H_{11}O_4Ag$. Calculated %: Ag 33.03.

Analysis of the Lactonic Acid:

Found %: C 65.55; H 5.49.

$C_{12}H_{12}O_4$. Calculated %: C 65.45; H 5.45.

4. Condensation with ortho chlorobenzaldehyde. 7 g of o-chlorobenzaldehyde is poured into an "Ott reagent," prepared with 5.2 g of malonic acid, and then is treated as described above. This yields 1.5 g of the β-lactone of o-chlorobenzal-malonic acid as a white crystalline substance with a m.p. of 123-123.5° (from chloroform).

| | | |
|---|---|---|
| | Titration: 0.1135 g substance: | |
| | Consumed: 0.1N NaOH in the cold ..... | 5.00 ml. |
| | Consumed: after boiling for 1 hour with alkali..... | 10.12 ml. |
| $C_{10}H_7O_4Cl$. | Computed: for neutralization ..... | 5.01 ml. |
| | Computed: for neutralization and saponification ... | 10.02 ml. |

The initial lactonic acid is not recovered after acidulation.

Analysis of the silver salt precipitated from a solution of the lactonic acid, neutralized with alkali in the cold, by silver nitrate:

Found %: Ag 32.08.

$C_{10}H_6O_4ClAg$. Calculated %; Ag 32.39.

Analysis of the Lactonic Acid:

Found %: C 52.79; H 3.24.

$C_{10}H_7O_4Cl$. Calculated %: C 52.99; H 3.09.

5. Condensation with para chlorobenzaldehyde. 7 g of p-chlorobenzaldehyde is poured into an "Ott reagent," prepared with 5.2 g of malonic acid, and then is treated as outlined above. This yields 1.1 g of the β-lactone of p-chlorobenzalmal-onic acid as a white crystalline substance with a m.p. of 145-155° (from an alcohol-acetone mixture).

| | | |
|---|---|---|
| | Titration: 0.0510 g substance: | |
| | Consumed: 0.1N NaOH in the cold ..... | 2.2 ml. |
| | Consumed: after boiling for 1 hour with alkali ... | 4.45 ml. |
| $C_{10}H_7O_4Cl$. | Computed: for neutralization ..... | 2.24 ml. |
| | Computed: for neutralization and saponification .. | 4.48 ml. |

The initial lactonic acid is not recovered by acidulation.

Analysis of the silver salt:

Found %: Ag 32.07.

$C_{10}H_6O_4ClAg$. Calculated %: Ag 32.39.

Analysis of the Lactonic Acid.

Found %: C 52.75; H 2.91.
$C_{10}H_7O_4Cl$. Calculated %: C 52.99; H 3.09.

6. Condensation with meta chlorobenzaldehyde. 8 g of m-chlorobenzaldehyde is poured into an "Ott reagent," prepared with 6 g of malonic acid, and then is treated as set forth above. This yields 2.5 g of the β-lactone of m-chlorobenzal-malonic acid as a white crystalline substance with a m.p. of 161-162° (from an alcohol-benzene mixture).

Titration: 0.0915 g substance:

| | | |
|---|---|---|
| | Consumed: 0.1N NaOH in the cold ..... | 4.10 ml. |
| | Consumed: after boiling for 1 hour with alkali ..... | 8.15 ml. |
| $C_{10}H_7O_4Cl$. | Computed: for neutralization ..... | 4.04 ml. |
| | Computed: for neutralization and saponification .... | 8.08 ml. |

The initial lactonic acid is not recovered after acidulation.

Analysis of the silver salt:
Found %: Ag 32.43.
$C_{10}H_6O_4ClAg$. Calculated %: Ag 32.39.

Analysis of the lactonic acid:
Found %: C 52.28; H 3.39.
$C_{10}H_7O_4Cl$. Calculated %: C 52.99; H 3.09.

7. Condensation with diacetone alcohol. 20 g of diacetone alcohol is poured into the "primary mixed anhydride", prepared from 10 g of malonic acid (cf Report V, Experiment 3) [1], and then is treated as set forth above. This yields 4 g of the acid ester of diacetone alcohol and malonic acid, as a light-yellow water-soluble oil with a sharp odor.

Titration: 0.1670 g substance:

| | | |
|---|---|---|
| | Consumed: 0.1 N NaOH in the cold ..... | 8.36 ml. |
| | Consumed: after boiling for 3 hours with alkali ... | 16.45 ml. |
| $C_8H_{14}O_5$. | Computed: for neutralization ..... | 8.26 ml. |
| | Computed: for neutralization and saponification .. | 16.52 ml. |

It produces a semicarbazone with a m.p. of 232-234° (from alcohol).

Titration of the semicarbazone: 0.1320 g substance:

| | | |
|---|---|---|
| | Consumed: 0.1N NaOH in the cold ..... | 5.20 ml. |
| | Consumed: after boiling for 3 hours with alkali ... | 10.35 ml. |
| $C_{10}H_{17}O_5N_3$. | Computed: for neutralization ..... | 5.09 ml. |
| | Computed: for neutralization and saponification ... | 10.18 ml. |

Found %: N 16.32.
$C_{10}H_{17}O_5N_3$. Calculated %: N 16.21.

8. Condensation with acetaldehyde. 15 g of paraldehyde is poured into the "primary mixed anhydride" prepared with 10 g of malonic acid, and then is treated as set forth above. This yields 4.5 g of the acid ester of acetaldol and malonic acid as a mobile oil, which is titrated with alkali in the cold and forms a silver mirror and a semicarbazone with a m.p. of 152-154° (from alcohol).

Titration: 0.1928 g substance:

| | | |
|---|---|---|
| | Consumed: 0.1N NaOH in the cold..... | 11.4 ml. |
| | Consumed: after boiling for 2 hours with alkali .... | 22.2 ml. |
| $C_7H_{10}O_5$. | Computed: for neutralization ..... | 11.1 ml. |
| | Computed: for neutralization and saponification .... | 22.2 ml. |

Titration of the semicarbazone: 0.0210 g substance:

| | | |
|---|---|---|
| | Consumed: 0.1N NaOH in the cold | 0.95 ml. |
| | Consumed: after boiling for 3 hours with alkali | 1.78 ml. |
| $C_9H_{13}O_5N_3$. | Computed: for neutralization | 0.91 ml. |
| | Computed: for neutralization and saponification | 1.82 ml. |

Found %: N 18.28. $C_9H_{13}O_5N_3$. Computed %: N 18.18.

The reaction with acetaldehyde is similar, as is the reaction of acetyl chloride with neutral silver malonate in the presence of acetaldehyde.

9. Condensation with propionic aldehyde. 20 g of propionic aldehyde is poured into the "primary mixed anhydride," prepared with 10 g of malonic acid, and then is treated as set forth above. This yields 5 g of the acid ester of propaldol and malonic acid, as a yellow-orange oil that forms a silver mirror and a semicarbazone with a m.p. of 177-179° (from alcohol).

Titration: 0.1212 g substance:

| | | |
|---|---|---|
| | Consumed: 0.1N NaOH in the cold | 6.1 ml. |
| | Consumed: after boiling for 2 hours with alkali | 12.08 ml. |
| $C_9H_{14}O_5$. | Computed: for neutralization | 6.0 ml. |
| | Computed: for neutralization and saponification | 12.0 ml. |

Titration of the semicarbazone: 0.0490 g substance:

| | | |
|---|---|---|
| | Consumed: 0.1N NaOH in the cold | 1.95 ml. |
| | Consumed: after boiling for 3 hours with alkali | 3.90 ml. |
| $C_{10}H_{17}O_5N_3$. | Computed: for neutralization | 1.89 ml. |
| | Computed: for neutralization and saponification | 3.77 ml. |

Found %: N 16.35. $C_{10}H_{17}O_5N_3$. Computed %: N 16.21.

10. Condensation with acetoacetic ester. 45 g of acetoacetic ester is poured into an "Ott reagent," prepared with 30 g of malonic acid, and then treated as set forth above. This yields 15 g of the acid ester of the enolic form of a acetoacetic ester and malonic acid, as a yellow oil.

Titration: 0.1338 g substance:

| | | |
|---|---|---|
| | Consumed: 0.1N KOH in the cold | 6.25 ml. |
| | Consumed: after boiling for 3 hours with alkali | 18.40 ml. |
| $C_9H_{12}O_6$. | Computed: for neutralization | 16.19 ml. |
| | Computed: for neutralization and saponification | 18.58 ml. |

It yields a p-nitrobenzyl ester with a m.p. of 202.5-204°.

Found %: N 5.76, 5.70.

$C_{23}H_{22}O_{10}N_2$. Calculated %: N 5.76.

11. Condensation with mesityl oxide. 15 g of mesityl oxide is poured into an "Ott reagent," prepared with 10 g of malonic acid, and then treated as set forth above. This yields 3 g of the acid ester of the enolic form of mesityl oxide and malonic acid, as a noncrystallizing, yellow-orange oil.

Titration: 0.1974 g substance:

| | | |
|---|---|---|
| | Consumed: 0.1N NaOH in the cold | 9.8 ml. |
| | Consumed: after boiling for 2 hours with alkali | 19.7 ml. |
| $C_9H_{12}O_4$. | Computed: for neutralization | 9.75 ml. |
| | Computed: for neutralization and saponification | 19.50 ml. |

Analysis of the silver salt:

Found %: Ag 36.83.

$C_9H_{11}O_4Ag$. Calculated %: Ag 37.11.

The reaction with the "primary mixed anhydride" and when acetyl chloride is reacted with neutral silver malonate in the presence of mesityl oxide is similar.

12. Condensation with pseudoionone. 10 g of pseudoionone is poured into an "Ott reagent," prepared with 10 g of malonic acid, and then is treated as set forth above. This yields 3 g of the acid ester of the enolic form of pseudoionone and malonic acid, as a noncrystallizing orange oil.

Titration: 0.1616 g substance:

| | | |
|---|---|---|
| | Consumed: 0.1N NaOH in the cold | 5.9 ml. |
| | Consumed: after boiling for 1 hour with alkali | 11.75 ml. |
| $C_{16}H_{22}O_4$. | Computed: for neutralization | 5.81 ml. |
| | Computed: for neutralization and saponification | 11.62 ml. |

Analysis of the silver salt:

Found %: Ag 27.95.

$C_{16}H_{21}O_4Ag$. Calculated %: Ag 28.05.

The reaction with the "primary mixed anhydride" and when acetyl chloride is reacted with neutral silver malonate in the presence of pseudoionone is similar.

13. Condensation with benzalacetone. 15 g of fused benzalacetone is poured into an "Ott reagent," prepared with 10 g of malonic acid, and then is treated as set forth above. This yields 4 g of the acid ester of the enolic form of benzalacetone and malonic acid, as a noncrystallizing, yellow-orange oil.

Titration: 0.0498 g substance:

| | | |
|---|---|---|
| | Consumed: 0.1N NaOH in the cold | 2.38 ml. |
| | Consumed: after boiling for 1 hour with alkali | 4.73 ml. |
| $C_{13}H_{12}O_4$. | Computed: for neutralization | 2.37 ml. |
| | Computed: for neutralization and saponification | 4.74 ml. |

Analysis of the silver salt:

Found %: Ag 37.52.

$C_{13}H_{11}O_4Ag$. Calculated %: Ag 37.46.

14. Condensation with Chloral. 15 g of chloral is poured into an "Ott reagent," prepared with 10 g of malonic acid, and then is set aside for 24 hours. It is then poured into water. The oil that separates out is heavier than water; it is extracted with ether, and the ether solution is washed with water and desiccated, after which the ether is driven off, and the residue is distilled in vacuum. This yields 8 g of chloral diacetate, as a colorless oil with a b.p. of 111.5-112.5° at 10 mm or 98-99° at 6 mm; $d_4^{15}$ 1.4214.

Saponification: 0.1019 g substance:

| | | |
|---|---|---|
| | Consumed: after boiling for 10 minutes with an excess of 0.1N NaOH | 8.91 ml. |
| $C_8H_7O_4Cl_3$. | Computed: for saponification | 8.74 ml. |

15. 6.4 g of neutral silver malonate is added to 6 g of chloral, and 10 g of acetyl chloride is added drop by drop with constant stirring. The precipitate is filtered out, and the filtrate is set aside for a day. It is then poured into water, and the heavy oil that separates out is extracted with ether. The ether extract is washed with water and desiccated, and, after the ether has been driven off, the residue is distilled twice. This yields 3 g of chloral chloroacetate, as a colorless oily substance with a b.p. of 186-187°; $d_4^{15}$ 1.4773.

## SUMMARY

The condensation of neutral mixed malonic-acetic anhydride with a number of carbonyl compounds has been studied, and it has been found that:

a) Whenever the carbonyl compound contains a hydroxyl group in addition to the carbonyl group, or whenever the former group is formed as a result of the enol-

ization or aldolization of the carbonyl compound, malonates are formed instead of β-lactonic acids.

b) If a large proportion of the carbonyl compound consists of a resonance structure with local resonance at the carbonyl group, β-lactonic acids will be predominantly formed, inasmuch as such structures favor the addition of both the organic anion of the methylene component and the hydrogen ion.

c) Whenever there are large numbers of resonance structures in which the positive charge is not on the carbon atom of the carbonyl group, no condensation takes place at all.

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# THE ACTIVITY OF ALUMINUM CHLORIDE PREPARED BY THE RADSIWANOWSKI METHOD

## 1. THE EFFECT OF $AlCl_3$ PREPARED BY THE RADSIWANOWSKI METHOD UPON THE $C_6H_6 + C_2H_5Br$ REACTION

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In 1895 Radsiwanowski's original paper [1], "The Use of Metallic Aluminum and HCl Gas in the Synthesis of Aromatic Hydrocarbons," appeared. He substituted aluminum shavings and HCl gas for powdered aluminum chloride, which is extremely hygroscopic, in the syntheis of ethylbenzene, diphenylmethane, and other substances. His preliminary results demonstrated that such an aluminum chloride is an active catalyst for the synthesis of aromatic hydrocarbons. Notwithstanding the fact that syntheses with the "Radsiwanowski"* $AlCl_3$ are simpler, more convenient, and more economical than those employing ordinary aluminum chloride, this paper has been neglected up to the present time.

Year by year the list of syntheses as well as of types of reactions that can be effected with $AlCl_3$ grows longer. Surveys of these reactions with $AlCl_3$ have been given by Kraenzlein [5], Dobryansky [2], and Ellis, [3], and in the article by Egloff [4] and the monograph by Thomas [6].

We began our research on the activity of the $AlCl_3$ prepared by the Radsiwanowsky method by synthesizing ethylbenzene. We studied the effect of several factors, such as: differences in the amount of aluminum shavings, their purity, the length of treatment of the mixture (benzene + Al shavings) with HCl gas, and the time intervening until the reaction products are decomposed by water. We felt that such a detailed examination of the effect of various factors was advisable to obtain a clear picture of how the process takes place and to ascertain the optimum conditions for the production of ethylbenzene. Comparison of the results obtained under various process conditions enabled us to draw several inferences that are not contained in Radsiwanowski's paper.

We found that benzene is readily condensed with ethyl bromide when 2% of Al shavings (based on the benzene used in the reaction) are added instead of equimolecular quantities of the usual aluminum chloride. The yield of ethylbenzene is 73% when the reaction is carried out at 10-12°. Condensation is in accordance with the following general equation:

$$C_6H_6 + RX \longrightarrow C_6H_5R + HX,$$

but it is accompanied by the formation of polyalkylbenzenes, the isomerization of

* Henceforth the aluminum chloride prepared by the Radsiwanowski method will be denoted by the abreviation: $AlCl_3$ - R.

the products, and by cleavage reactions. This results in the production of a complex mixture of ethylated benzenes, ranging from monoethylbenzene to tetraethylbenzene, inclusive. The reaction mixture contains 72-73% of ethylbenzene, 16-18% of 1,3-diethylbenzene and a very minute quantity of 1,4-diethylbenzene, up to 6-10% of 1,3,5-triethylbenzene, and up to 3% of 1,2,4,5-tetraethylbenzene. The yields of the reaction end products were computed on the basis of the ethyl bromide placed in the reaction. The preponderance of 1,3-diethylbenzene in the mixture of 1,3- and 1,4-diethylbenzenes and 1,3,5-triethylbenzene can be explained on the basis of the theory proposed by Price [7] and of the hypothesis advanced by Anschutz [8] in agreement with Baddely and Kenner [9].

To determine the optimum conditions for the synthesis of ethylbenzene with "$AlCl_3$-R" in a Friedel Crafts reaction we investigated: the effect of the quantity of Al shavings; the rate of formation of "$AlCl_3$-R" from Al shavings and HCl gas, i.e., the time required for treating the "benzene + Al shavings" mixture with the HCl gas; the time the reagents are in contact, i.e., the time elapsing until the reaction mixture is decomposed with water; and the purity of the Al shavings.

A series of tests made with varying quantities of Al shavings (ranging from 1% to 10%, in terms of the benzene placed in the reaction) showed that the quantity of the catalyst affects the course and depth of the condensation. Comparison of the results obtained under otherwise identical conditions (Table 1) showed that the maximum yield of ethylbenzene was obtained with 2% of Al shavings added to the benzene. Any further rise in the percentage of Al shavings diminishes the yield of ethylbenzene and promotes more thoroughgoing condensation.

TABLE 1

Effect of the Quantity of Al Shavings on the Ethylbenzene Yield

| Quantity of Al shavings g | Ethylbenzene yield, % | Diethylbenzene yield, % | Triethylbenzene yield, % | Tetraethylbenzene yield, % | Remarks |
|---|---|---|---|---|---|
| 1 | 68 | 17 | 1 | - | In all the tests 40% of benzene was driven off, based on the amount of benzene placed in reaction. |
| 2 | 73 | 18 | 3 | A few drops | |
| 4 | 63 | 11 | 7 | Ditto | |
| 5 | 54 | 11 | 7 | 2 | |
| 5 | 43 | 12 | 8 | 3 | |
| 10 | 40 | 10 | 10 | 3 | |

Investigation of the rate at which "$AlCl_3$-R" is formed from Al shavings and HCl gas (Table 2) showed that 4 to 5 hours suffice for treating the mixture of benzene and Al shavings with HCl gas, all other conditions remaining the same (adding 2% of Al shavings and a temperature of 10-12°). Any further treatment of the mixture with HCl gas increases the quantity of dealkylation products.

The results of a series of tests run to ascertain the effect of the time the reagents are in contact upon the ethylbenzene yield indicated (Table 3) that the time elapsing until the reaction mixture is decomposed with water must be at least 48 hours.

It is stated in the literature that activated aluminum must be used in the preparation of aluminum chloride whenever Radsiwanowski aluminum chloride is used in a Friedel-Crafts reaction. The best method of activation is calcining the Al shavings at 300° for 30 minutes.

We ran a series of tests with Al shavings activated as indicated above. Our results showed that the preliminary activation of the Al shavings has absolutely no effect upon the process of preparing the "$AlCl_3$-R"; in our subsequent

research we therefore employed ordinary unactivated shavings.

## EXPERIMENTAL

All tests were made in a standard apparatus, consisting of a 500-ml round-bottomed flask fitted with a ground-in reflux condenser and a tube (likewise ground-in) reaching to the bottom of the flask for passing the HCl gas through. The flask was filled with 200 g of pure anhydrous benzene, and 4 g of aluminum shavings (2%), and a current of anhydrous HCl gas was passed through until the aluminum shavings were coated with a brown film. Then 100 g of freshly distilled ethyl bromide was added drop by drop, the flask being chilled by ice.

After the violent evolution of HBr gas had ended, the mixture was set aside

TABLE 2

Effect of the Time During Which the Reaction Mixture is Treated with HCl Gas Upon the Yield of Ethylbenzene

| Quantity of Al shavings, g | Duration of treatment with HCl gas, hours | Ethylbenzene, yield, % | Diethylbenzene, yield, % | Triethylbenzene yield, % | Tetraethyl benzene, yield, % | Remarks |
|---|---|---|---|---|---|---|
| 2 | 4:30 | 71 | 17-18 | 2.0 | a few drops | In all the tests, 40% of benzene was driven off, based on amount of benzene placed in reaction. |
| 2 | 5:00 | 73 | 17.0 | 2.0 | | |
| 2 | 9:00 | 73 | 14.0 | 2.0 | | |
| 2 | 12:00 | 75 | 6.0 | 2.0 | | |
| 2 | 15:00 | 74 | 5.0 | 2.0 | | |

TABLE 3

Effect of the Time During which the Reagents Are in Contact Upon the Yield of Ethylbenzene

| Quantity of Al shavings, g | Duration of treatment with HCl gas, hours | Duration of contact between reagents, hours | Ethylbenzene yield, % | Diethylbenzene yield, % | Triethylbenzene yield, % |
|---|---|---|---|---|---|
| 2 | 6 | 1 | - | - | - |
| 2 | 6 | 24 | 20.0 | 5.0 | - |
| 2 | 6 | 32 | 20.0 | 5.0 | - |
| 2 | 6 | 48-52 | 72.0 | 16.0-17.0 | 3.0 |
| 2 | 6 | 56-60 | 73.0 | 17.0 | 3.0 |

to stand at room temperature for 48 hours and then heated with a reflux condenser to the boiling point of benzene over a water bath for 2 hours. Upon cooling, the reaction products were decomposed with water, saponified, desiccated over $CaCl_2$, and then distilled twice into a herringbone dephlegmator. The following fractions were collected:

I: 132-134° — 73.0%
II: 180-182° — 18.0%
III: 212-214° — 2.5%
IV: 250-255° — 1.0%
V: Above 255° - 1.0%

The percentage yields are based on the amount of ethyl bromide placed in reaction.

In addition to the foregoing fractions, about 40% of benzene (based on the initial quantity placed in reaction) was driven off.

Fraction I

B.p. 132-134°; $d_4^{20}$ 0.8703; $n_D^{20}$ 1.4950; $MR_D$ 35.50.
$C_8H_{10}$. Computed: $MR_D$ 35.54.

0.5050 g substance: 20.01 g benzene: Δt 1.18°.
Found: M 109.0.
$C_8H_{10}$. Computed: M 106.08.

Synthesis of 2-nitro-1-ethylbenzene. 25 g of ethylbenzene was added gradually, during the course of 4 hours, in the cold to a mixture of 20.5 g of $HNO_3$ (d = 1.5) and 27 g of $H_2SO_4$ (d = 1.85), and the mixture was gradually heated to 135°. The resulting oily product was distilled. The bulk of the product, a heavy oil (d = 1.13), passes over at 224-227°; according to the literature, this corresponds to 2-nitro-1-ethylbenzene.

Fraction II.

B.p. 182-184°; $d_4^{20}$ 0.8605; $n_D^{20}$ 1.4892; $MR_D$ 44.44.
$(C_2H_5)_2C_6H_4$. Computed: $MR_D$ 44.78.

0.6032 g substance: 20.50 g benzene: Δt 1.10°.
Found: M 137.2.
$(C_2H_5)_2C_6H_4$. Computed: M 134.11.

Synthesis of 2,4,6-trinitro-1,3-diethylbenzene. Nitration of a mixture of $HNO_3$ and $H_2SO_4$ (the nitrating mixture was poured into the hydrocarbon) yielded a crystalline product that exhibited a m.p. of 62-63° after recrystallization from ethanol, which corresponds to 2,4,6-trinitro-1,3-diethylbenzene according to Voswinkel [10].

It was possible that the 182-184° fraction was a mixture of para and meta diethylbenzenes. The mixture was separated by the Voswinkel method [11]. This was done by dissolving the 182-184° fraction in slightly fuming sulfuric acid. A few pieces of ice were cautiously added, and the liquid sulfo acids were separated out and then saturated with barium carbonate. The resulting barium-1,3- and 1,4-diethylbenzosulfonates were recrystallized from water. The precipitate was separated from the mother liquor. The Ba salt of 1,3-diethylbenzosulfonic acid is hardly soluble in $H_2O$; the Ba salt of 1,4-diethylbenzosulfonic acid is very highly soluble. Evaporation of the mother liquor yielded a very small quantity (5-7% of the weight of the precipitate) of the Ba salt of 1,4-diethylbenzosulfonic acid.

The precipitate is the Ba salt of 1,3-diethylbenzosulfonic acid. In view of the fact that the 182-184° fraction is mostly 1,3-diethylbenzene, the mixture of the 1,3- and 1,4-diethylbenzene isomers was not separated in later operations.

Fraction III.

B.p. 212-214°; $d_4^{20}$ 0.8702; $n_D^{20}$ 1.4963; $MR_D$ 54.65.
$(C_2H_5)_3C_6H_3$. Computed: $MR_D$ 54.02.

0.6503 g substance: 19.801 g benzene: Δt 1.04°.
Found: M 160.0.
$(C_2H_5)_3C_6H_3$. Computed: M 162.

The 212-214° fraction corresponds to 1,3,5-triethylbenzene; this was proved by the synthesis of its nitro derivative: nitration of the fraction by a nitrating mixture yielded a yellow crystalline substance. Recrystallization from dilute ethanol yielded crystals with a m.p. of 108°, i.e, a substance that corresponded

to 2,4,6-trinitro-1,3,5-triethylbenzene, according to Gatterman [12]

Fraction IV

B.p. 250-255°; $d_4^{20}$ 0.8680; $n_D^{20}$ 1.5091; $MR_D$ 65.37.

$(C_2H_5)_4C_6H_2$. Computed: $MR_D$ 64.25.

0.3208 g substance: 19.80 g benzene: $\Delta$ t 0.43°.
Found: M 191.2.
$(C_2H_5)_4C_6H_2$. Computed: M 190.0.

The 250-255° fraction was not analyzed any further, inasmuch as the quantity of product recovered was extremely small. Nor was the tarry residue analyzed.

## SUMMARY

Aluminum chloride prepared by the Radsiwanowski method is an active catalyst in the Friedel-Crafts synthesis of ethylbenzene.

The catalytic action of "$AlCl_3$-R" upon a mixture of benzene and ethyl bromide is accompanied by a number of side reactions: condensation, dissociation, and isomerization. These reactions often overlap, resulting in a complex mixture of the reaction end products.

Transfer of the alkyl group is accompanied by the formation of di-, tri-, and tetraalkylbenzenes.

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# REACTIONS WITH ALUMINUM CHLORIDE PREPARED BY THE RADSIWANOWSKI METHOD

## CONDENSATION OF BENZENE WITH SOME UNSATURATED ALIPHATIC HALOGEN DERIVATIVES AND POLYHALOGEN DERIVATIVES

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The present paper discusses the results of condensing benzene with unsaturated alkyl halides, dihalides, and polyhalides over $AlCl_3$ prepared by the Radsiwanowski method. We investigated the following alkyl and alkene halides: 1,2-dichloro- and 1,2-dibromoethane; 2-methyl-1,2-dibromopropane (isobutylene bromide); 2-methyl-3-chloropropene-1; allyl chloride; 1,2,3-tribromopropane; 2-methyl-1,2,3-tribromopropane; 2-methyl-1,2-dibromo-3-chloropropane; 1,1,2,2-tetrachloroethane; and tetrachloroethylene.

Some of the above-mentioned condensations were effected with ordinary $AlCl_3$, as has been described in the literature; the condensation of benzene with 2-methyl-3-chloropropene-1, 2-methyl-1,2,3-tribromopropane; and 2-methyl-1,2-dibromo-3-chloropropane have been effected for the first time. None of the above-mentioned reactions had ever been carried out with $AlCl_3$-R.*

The condensations discussed here were effected under various conditions with $AlCl_3$-R (varying proportions of benzene and halogen derivatives, varying reaction temperatures, different percentages of Al, and varying reaction times). The reaction of dichloroethane with benzene in the presence of aluminum chloride was investigated by Silva [5] in 1879. The principal reaction product was 1,2-diphenylethane, plus some ethylbenzene:

$$CH_2ClCH_2Cl + 2C_6H_6 \longrightarrow C_6H_5CH_2CH_2C_6H_5 + 2HCl.$$

$$C_6H_5CH_2CH_2C_6H_5 + 2H \longrightarrow C_6H_6 + C_6H_5CH_2CH_3.$$

Interest has been reawakened in this reaction recently. Mention should be made at this point of the researches of the Russian scientists Klebansky [1] and Korshak [2]. We have studied this reaction in the presence of $AlCl_3$-R. We have found that, on the whole, the process is the same as that with ordinary aluminum chloride. It is worthy of note that when we condensed 1,2-dichloroethane with benzene, we also recovered a minute quantity of 1,1-diphenylethane, apparently as a product of the isomerization of 1,2-diphenylethane by the $AlCl_3$-R. The reaction of 1,2-dibromoethane with benzene is quite similar.

Bodroux [6] explored the condensation of 2-methyl-1,2-dibromopropane with

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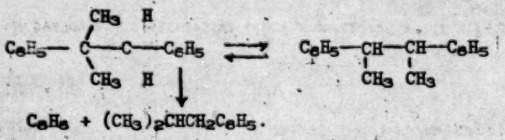
* The aluminum chloride prepared by the Radsiwanowski method will henceforth be denoted by the abbreviation $AlCl_3$.

benzene in the presence of ordinary $AlCl_3$, finding the principal reaction product to be 1,1-dimethyl-1,2-diphenylethane. Some butylbenzene was also recovered as a cracking product, together with a minute amount of some crystalline substance, which the author was unable to isolate.

We performed this condensation in the presence of $AlCl_3$-R, recovering the same end products as Bodroux. The crystalline substance proved to be 1,2-dimethyl--1,2-diphenylethane, i.e., an isomer of the principal reaction product.

The isomerization of 1,1-dimethyl-1,2-diphenylethane to symmetrical 1,2-dimethyl-1,2-diphenylethane was proved by us experimentally: a current of anhydrous HCl gas was passed through a benzene solution of 1,1-dimethyl-1,2-diphenylethane with 2% Al for several hours. Almost 50% of 1,2-dimethyl-1,2-diphenylethane was found in the end product. Thus what happens here is the migration of a $CH_3$ group from one carbon atom to its neighbor. This is paralleled by cracking, giving rise to isobutylbenzene:



$C_6H_6 + (CH_3)_2CHCH_2C_6H_5$.

The yields of 1,1-dimethyl-1,2-diphenylethane obtained with $AlCl_3$-R are higher than those with ordinary aluminum chloride.

We are the first to have explored the reaction of 2-methyl-2-chloropropene-1 with benzene. This yielded: crystalline 1,2-dimethyl-1,2-diphenylethane; liquid 1,1-dimethyl-1,2-diphenylethane; and isobutylbenzene; the nature of the latter was established by bromination by the Schramm method [9]. The reaction of the initial product with benzene may be depicted as occurring in several stages.

a) $CH_2=C(CH_3)CH_2Cl + C_6H_6 \longrightarrow CH_2=C(CH_3)CH_2C_6H_5 + HCl$

b) $CH_2=C(CH_3)CH_2C_6H_5 + HCl \longrightarrow CH_3CCl(CH_3)-CH_2-C_6H_5$

c) $(CH_3)_2CClCH_2C_6H_5 + C_6H_6 \longrightarrow (CH_3)_2C(C_6H_5)-CH_2-C_6H_5$

d) $C_6H_5C(CH_3)_2CH_2C_6H_5 \rightleftharpoons C_6H_5CH(CH_3)CH(CH_3)C_6H_5$.

The condensation of allyl chloride with benzene in the presence of $AlCl_3$-R proved to be a similar process. Konovalov and Dobrovolsky [3] effected this condensation with ordinary aluminum chloride, finding that a mixture of diphenylpropanes resulted. Under our conditions, using $AlCl_3$-R, the following were recovered: propylbenzene and diphenylpropane as an oil with intense lilac fluorescence. The reaction is as follows:

a) $CH_2=CHCH_2Cl + C_6H_6 \longrightarrow CH_2=CHCH_2C_6H_5 + HCl$.

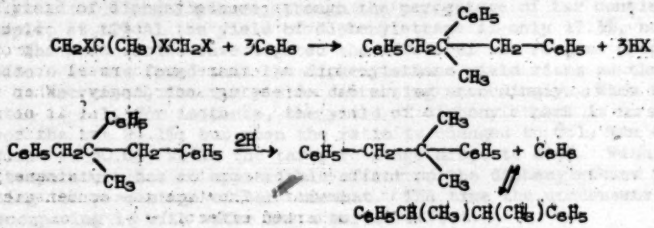
b) $CH_2=CHCH_2C_6H_5 + HCl \longrightarrow CH_3CHClCH_2C_6H_5$

c) $CH_3CHClCH_2C_6H_5 + C_6H_6 \longrightarrow C_6H_5CH(CH_3)CH_2C_6H_5 + HCl$.

Of the trihalogen derivatives, 1,2,3-tribromopropane was chosen for condensation with benzene. This condensation was effected in 1885 by Claus and Merklin [7], using ordinary aluminum chloride. They recovered some 1,2,3-triphenylpropane

(as a liquid that boiled at above 340° with decomposition), and 1,3-diphenylpropane as the principal product. Above $AlCl_3$-R we got about 10% of 1,3-diphenylpropane, no triphenylpropane being found.

We then tested $AlCl_3$-R in the condensation of 2-methyl-1,2,3-tribromopropane and 2-methyl-1,2-dibromo-3-chloropropane with benzene. The two reactions were similar, yielding the same products. As in the preceding cases, no triphenylpropane product was found, only two substances being recovered, one liquid and one crystalline: 1,1-dimethyl-1,2-diphenylethane and 1,2-dimethyl-1,2-diphenylethane. There was more of the solid product than of the liquid isomer. Thus, the foregoing condensations may be represented by the following diagram:



The tetrahalogen derivative used for condensation with benzene was 1,1,2,2-tetrachloroethane. We know from the literature that anthracene is formed in this condensation [8].

Tetrachloroethane condenses with difficulty with benzene at room temperature in the presence of $AlCl_3$-R, only a negligible quantity of anthracene being recovered. At a higher temperature, (70-75°) and with more of the catalyst used, 1,2-diphenylethane is formed:

$$CHCl_2CHCl_2 + 4C_6H_6 \longrightarrow (C_6H_5)_2CHCH(C_6H_5)_2 + {}_4HCl.$$

$$(C_6H_5)_2CHCH(C_6H_5)_2 + 4H \longrightarrow 2C_6H_6 + C_6H_5CH_2CH_2C_6H_5.$$

Thus, either the intermediate tetraphenyl derivative is destructively hydrogenated or the tetrahalogen derivative is first reduced to a 1,2-dihalogen ethane which is then condensed with benzene.

We were unable to effect the condensation of benzene with tetrachloroethylene in the presence of $AlCl_3$-R no matter what experimental conditions were used. According to Mouneyrat [10], this condensation at 70° in the presence of ordinary aluminum chloride results in the formation of some anthracene.

Generalizing these results, we may draw the following conclusion: 1) on the whole, condensation with $AlCl_3$-R is the same as condensation with ordinary aluminum chloride; 2) the yields of the corresponding phenylated derivatives drops appreciably as the number of halogen atoms in the respective halogen derivatives is increased; 3) if the number of halogen atoms in the molecule of the halogen derivative remains the same, the yield of phenylated products rises somewhat when a methyl side group is present; 4) it has been found that, as a rule, the condensation of tri- and tetrahalogen derivatives with benzene is accompanied by cracking and only the mono- and diphenyl derivatives are synthesized in the presence of $AlCl_3$-R; 5) the condensations are combined with isomerizations; 6) unsaturated monohalogen derivatives also yield diphenylated products as the result of the addition of HCl at the double bond; and 7) the halogen atoms practically do not react at the double bond (in the presence of $AlCl_3$-R).

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1. X denotes a halogen (Br or Cl).

## EXPERIMENTAL

The method of condensing halogen derivatives with benzene in the presence of $AlCl_3$-R is essentially the same as in the previous report, and we shall therefore omit it here.

1. Condensation of 1,2-dichloroethane with benzene. Four series of tests were made to determine how various factors affected the course of condensation. In the first series we studied the effect of the amount of catalyst (% of Al shavings) on the yield of reaction products. The optimum figure was found to be 2% Al (yield: 25.2% of 1,2-diphenylethane and 10.1% of tar). Raising the percentage of catalyst diminishes the yield of diphenylethane, though the percentage of tar continues to rise. For example, at 12% Al the yield of diphenylethane is only 17.3%, but that of the tar 39.1%. The next series investigated the effect of the reagent proportions upon the reaction. It was found that the diphenylethane yield rises as the percentage of benzene is increased, the tar yields decreasing accordingly. When the chloride:benzene ratio is 1:1, for instance, the yield of diphenylethane is no more than 6.5% and that of the tar 24.1%; but when the ratio is changed to 8:1, the diphenylethane yield rises to 30.6%, while the tar percentage drops to 2.9%. Within the 16-80° range, temperature has no appreciable effect on the diphenylethane yield, merely increasing the percentage of tar somewhat. The time the condensate is kept before decomposing it with water has a marked effect.

Keeping it for 2 hours gives a diphenylethane yield of 4% and a tar yield of 1.2%.

Keeping it for 24 hours gives a diphenylethane yield of 25.2% and a tar yield of 7.6%.

Keeping it for 48 hours gives a diphenylethane yield of 26.2% and a tar yield of 14%.

It is obviously best to wait 24 hours before decomposing the condensate with water, as any longer storage merely promotes the formation of tar. The residue recovered after the benzene was driven off was distilled, the diphenylethane fraction (265-290°) being recovered from it. After purification and recrystallization from alcohol, the diphenylethane fused at 51.5-52° and had an M = 178.1 (the calculated molecular weight of $C_{14}H_{14}$ = 182.2).

0.1105 g substance: 0.3728 g $CO_2$; 0.0762 g $H_2O$.
0.0984 g substance: 0.3318 g $CO_2$; 0.689 g $H_2O$.
Found %: C 91.92, 91.96; H 7.71, 7.83.
$C_{14}H_{14}$. Computed %: C 92.25; H 7.75.

Further fractional distillation of the 260-290° fraction yielded a liquid with a b.p. of 272-278° and an unpleasant odor, asymmetrical 1,1-diphenylethane. Its constants were as follows:

$d_4^{18}$ 1.0049; $n_D^{18}$ 1.57428; M 180.1; $MR_D$ 59.69.
$C_{14}H_{14}$. Computed: $MR_D$ 59.65.
0.0893 g substance: 0.3014 g $CO_2$; 0.0627 g $H_2O$.
0.1076 g substance: 0.3628 g $CO_2$; 0.0757 g $H_2O$.
Found %: C 92.05, 91.95; H 7.85, 7.87.
$C_{14}H_{14}$. Computed %: C 92.25; H 7.75.

The results of our condensation of 1,2-dibromoethane with benzene were practically the same as when dichloroethane was used, and we therefore shall dispense with the details here.

2. Condensation of isobutylene bromide with benzene. This condensation was performed under the following conditions: bromide:benzene ratio of 1:4; 2% Al (based on the benzene); room temperature; and storage for 25 hours. After decomposition with water and desiccation of the oily layer with $CaCl_2$, the benzene was driven off, and the residue was separated into the following fractions:

Fraction I (90-160°): 4 g*
Fraction II (167-179°): 6.5 g.
Fraction III (260-293°): 28.82 g.
A solid cake of residue remained in the flask.

Fraction I is the initial dibromide with traces of the decomposition products and benzene; it exhibits a clear halogen reaction. Fraction II proved to be a mixture of isobutyl- and tert.-butylbenzenes, with the general formula of $C_6H_5C_4H_9$. Bromination of the product in direct sunlight, by the Schramm method [9], enabled us to show that the mixture contained 89% of the tertiary isomer, produced by the isomerization of the isobutylbenzene.

Cryoscopic determination of the molecular weight in benzene yielded two figures: 135.3 and 132.7 (the calculated value for $C_6H_5C_4H_9$ is 134.1).

$d_4^{14}$ 0.8680; $n_D^{14}$ 1.49166; $MR_D$ 44.81.
$C_{10}H_{14}$. Computed: $MR_D$ 44.78.
0.0816 g substance: 0.2672 g $CO_2$; 0.0764 g $H_2O$.
0.0761 g substance; 0.2844 g $CO_2$; 0.0723 g $H_2O$.
Found %: C 89.30, 89.16; H 10.47, 10.83.
$C_{10}H_{14}$. Computed %: C 89.49; H 10.51.

Repeated fractionation of Fraction III yielded an oil with a b.p. of 284-288°, which proved to be the principal reaction product, 1,1-dimethyl-1,2-diphenylethane, described by Bodroux [8].

$d_4^{17}$ 0.9815; $n_\alpha^{22}$ 1,54889; $n_D^{17}$ 1.55632; $MR_\alpha$ 69.08; $MR_D$ 68.81.
Found: M 207.9, 205.5;
$C_{16}H_{18}$. Computed: $MR_\alpha$ 69.38; $MR_D$ 68.88; M 210.3.
0.1404 g substance: 0.46 g $CO_2$, 0.1381 g $H_2O$.
0.1093 g substance: 0.3653 g $CO_2$; 0.0859 g $H_2O$.
Found %: C 91.04, 91.15; H 8.74, 8.79.
$C_{16}H_{18}$. Computed %: C 91.37; H 8.63.

The yield of 1,1-dimethyl-1,2-diphenylethane is as much as 45% of the theoretical. The results of the tests were not affected significantly by changes in the experimental conditions. It was found that Fraction III also contained negligible quantities of a crystalline substance. We succeeded in isolating this latter in a quantity sufficient for analysis by means of repeated tests. It was found that the yields could be raised from 0.1-0.2 g to 0.4-0.45 g by effecting condensation at higher temperature (60-70°). The substance was recrystallized from alcohol and had a m.p. of 125°.

0.894 g substance: 0.2985 g $CO_2$; 0.0702 g $H_2O$.
Found %: C 91.06; H 8.78; M 208.6, 209.1.
$C_{16}H_{18}$. Computed %: C 91.37; H 8.63; M 210.3.

These figures indicate that the crystalline product is obviously an isomer of the liquid 1,1-dimethyl-1,2-diphenylethane.

To establish its structure, the crystalline substance was oxidized by $CrO_3$ as proposed by Lepin [4]. This yielded acetophenone, which was identified as its semicarbazone, with a m.p. of 199-200°, and we can therefore state that the substance

* 89 g of isobutylene bromide was used.

we isolated has a symmetrical structure and is 1,2-dimethyl-1,2-diphenylethane.

0.1061 g substance: 22.1 ml $N_2$ (18°, 752 mm).
Found %: N 23.93.
$C_9H_{11}ON_3$. Computed %: N 23.71.

To clear up the origin of this substance, 15 g of 1,1-dimethyl-1,2-diphenylethane was dissolved in 100 g of benzene with a Radziwanowski catalyst prepared from 2 g of Al. The mixture was allowed to stand for 30 hours at 15-18°. After the benzene had been driven off, the condensate was fractionated in vacuum:

Fraction I (37-40°, 7-8 mm): 2.4 g – a transparent liquid with the odor of butylbenzene.

Fraction II (114-140°, 6 mm): 7.3 g – a light-yellow oil.

Fraction III (148-170°, 6 mm): 3.2 g – a dark-yellow oil.

Some crystals with a m.p. of 124° were deposited on the walls of the receivers for Fractions II and III. When immersed in an ice-salt mixture, Fraction II was converted into a solid mass of crystals, but the other fractions underwent no change. Lepin [4] oxidation of 2 g of Fraction II yielded acetophenone (semicarbazone with a m.p. of 200°).

0.0948 g substance: 19.6 ml $N_2$ (16°, 750 mm).
0.0782 g substance: 16.3 ml $N_2$ (17°, 749 mm).
Found %: N 23.83, 23.88.
$C_9H_{11}ON_3$. Computed %: N 23.71.

This experiment confirmed our hypothesis that the asymmetrical isomer had been isomerized to the symmetrical one.

The substance recovered from Fraction II had a m.p. of 8-10°.

$d_{18}^{18}$ 0.9928; $n_D^{18}$ 1.56598; $MR_D$ 69.09; M 214.2, 209.9.
$C_{16}H_{18}$. Computed $MR_D$ 68.88; M 210.3.
0.1092 g substance; 0.3646 g $CO_2$; 0.0850 g $H_2O$.
0.0809 g substance: 0.2703 g $CO_2$; 0.0632 g $H_2O$.
Found %: C 91.06, 91.12; H 8.71, 8.74.
$C_{16}H_{18}$. Computed %: C 91.37; H 8.63.

Hence, Fraction II is a low-melting modification of 1,2-dimethyl-1,2-diphenylethane.

Closer analysis indicated that Fraction I was isobutylbenzene (result of cracking). Fraction III was the unchanged initial substance. Isomerization was about 50% complete. These results bear out Bodroux's data on the existence of two isomeric dimethyldiphenylethanes.

3. Condensation of 2-methyl-3-chloropropene-1 with benzene. This condensation was performed under the following conditions: ratio of the chlorine derivative to the benzene was 1:4 (32 + 100 g); room temperature; 2% of Al (based on the benzene); and storage for 23 hours. The condensate recovered after the benzene had been driven off was fractionated as follows:

Fraction I (160-180°): 7.2 g – a colorless oil
Fraction II (260-290°): 10.0 g – a cloudy yellow oil
Fraction III (290°): 3.8 g – a brown tar.

A butylbenzene was recovered from Fraction I that exhibited 80% of tert.-butylbenzene when brominated by the Schramm method [8]. Upon standing, a crystalline layer separated out from Fraction II. The crystals had a m.p. of 125° after

recrystallization from alcohol and exhibited no depression of the melting point when mixed with 1,2-dimethyl-1,2-diphenylethane. About 1 g of the crystals was recovered. The liquid part of this fraction consisted of 1,1-dimethyl-1,2-diphenylethane.

$d_4^{15}$ 0.9808; $n_D^{15}$ 1.55635; M 203.5; $MR_D$ 68.85.

$C_{16}H_{18}$. Computed: $MR_D$ 68.88; M 210.3.

0.1248 g substance: 0.4169 g $CO_2$; 0.0981 g $H_2O$.
0.1308 g substance: 0.4386 g $CO_2$; 0.1030 g $H_2O$.
Found %: C 91.10, 91.45; H 8.79, 8.81.
$C_{16}H_{18}$. Computed %: C 91.37; H 8.63.

4. Condensation of allyl chloride with benzene. The conditions for this condensation were similar to those employed in the preceding condensations. Fractionation of the condensate after the benzene had been driven off yielded the following fractions: -

Fraction I (148-152°): 1.9 g - a colorless liquid;
Fraction II (266-290°): 14.8 g - a liquid with lilac fluorescence;
Fraction III (above 300°): 10.6 g - a thick, dark-brown tar.

Repeated fractionation of Fraction I yielded an oil that boiled at 148-150° and proved to be propylbenzene.

$d_4^{18}$ 0.8660; M 123; $n_D^{18}$ 1.49381; $MR_D$ 40.31.
$C_9H_{12}$. Computed: $MR_D$ 40.16; M 120.

0.0981 g substance: 0.3223 g $CO_2$; 0.0897 g $H_2O$.
0.0915 g substance: 0.3009 g $CO_2$; 0.0827 g $H_2O$.
Found %: C 89.60, 89.69; H 10.23, 10.08.
$C_9H_{12}$. Computed %: C 89.85; H 10.15.

Repeated fractionation of Fraction II yielded a liquid that boiled at 279-281° and exhibited the beautiful lilac fluorescence of diphenylpropane. We did not investigate the structure of the product in greater detail.

$d_4^{18}$ 0.9804; $n_D^{18}$ 1.55665; $MR_D$ 64.36; M 192.
$C_{15}H_{16}$. Computed: $MR_D$ 64.26; M 196.3.

0.1203 g substance: 0.4039 g $CO_2$; 0.0801 g $H_2O$.
0.1074 g substance: 0.3604 g $CO_2$; 0.0796 g $H_2O$.
Found %: C 91.56, 91.51; H 8.38, 8.29.
$C_{15}H_{16}$. Computed %: C 91.78; H 8.22.

5. Condensation of 1,2,3-tribromopropane with benzene. The condensation conditions were: ratio of the tribromide to the benzene - 1:6; 2% Al (based on the benzene); room temperature; and storage for 20 hours. As a result some 10% of diphenylpropane was recovered from the condensate; none of the expected triphenylpropane was found. The diphenylpropane recovered was a colorless liquid with a b.p. of 295°.

$d_4^{18}$ 1.0202; $n_D^{18}$ 1.57904; $MR_D$ 63.72; M 192.
$C_{15}H_{16}$. Computed: $MR_D$ 64.26; M 196.27.

0.0882 g substance: 0.2958 g $CO_2$; 0.0655 g $H_2O$.
0.0768 g substance: 0.2579 g $CO_2$; 0.0573 g $H_2O$.
Found %: C 91.46, 91.58; H 8.31, 8.35.
$C_{15}H_{16}$. Computed %: C 91.78; H 8.22.

6. Condensation of 2-methyl-1,2,3-tribromopropane with benzene. We used 100 g of benzene and 63 g of the bromide, the ratio of the latter to the benzene being 1:6, the other conditions being: room temperature, 2% of Al, and storage for 20 hours.

After decomposition with water and driving off the benzene, we distilled the condensate in vacuum (5 mm):

Fraction I (82-85°) : 5.3 g – 8.4% (based on the tribromide);
Fraction II (110-112°) : 15.0 g – 33.4% (based on $C_{16}H_{18}$).

11.4 g (12.4% of the condensate) of a thick, dark tar remained in the flask. Fraction I proved to be the unreacted initial tribromide. Fraction II, after standing overnight, yielded 10 g of crystals (65% of the fraction), which exhibited a m.p. of 125° after recrystallization from alcohol and caused no depression when mixed with 1,2-dimethyl-1,2-diphenylethane.

0.0971 g substance: 0.3246 g $CO_2$; 0.0754 g $H_2O$.
0.1102 g substance: 0.3679 g $CO_2$; 0.0863 g $H_2O$.
Found %: C 91.26, 91.15; H 8.69, 8.75.
$C_{16}H_{18}$. Computed %: C 91.37; H 8.63.

7. Condensation of 2-methyl-1,2-dibromo-3-chloropropane with benzene. The conditions used for this condensation were similar to those used previously. Likewise, we obtained a 108-111° (5 mm) fraction, which yielded 8 g of crystals after standing for 24 hours; these crystals proved to be 1,2-dimethyl-1,2-diphenylethane, as they exhibited no depression when mixed with the latter.

8. Condensation of 1,1,2,2-tetrachloroethane with benzene. The reagents were used in a 1:6 chloride-benzene ratio. The condensation was performed at 20° for 20 hours. After the benzene and the unreacted original chloride had been driven off, a small quantity of condensate was recovered. From the latter we recovered 0.5 g of a crystalline substance with a m.p. of 208-209.5°. The molecular weight was found to be 176 cryoscopically in benzene (mol. wt. of anthracene = 178).

When the reaction is carried out at 70-75° with 6% of Al (based on the weight of benzene), the condensation proceeds differently. The products yielded 2.8 g of a crystalline substance with a m.p. of 51.5°, which exhibited no depression when mixed with 1,2-diphenylethane.

9. Condensation of tetrachloroethylene with benzene. The reagents were used in a 1:6 $C_2Cl_4$ – $C_6H_6$ ratio; the condensations were effected with 2,4,6,8, and 10% of Al at temperatures ranging from 19 to 70°. No condensation took place under any of these conditions, inasmuch as the initial substances were recovered unchanged from the condensate.

## SUMMARY

1. It has been shown that $AlCl_3$-R acts like ordinary aluminum chloride in promoting the processes of cleavage and isomerization in condensation reactions.

2. It has been found that an increase in the number of halogen atoms in the halogen derivative reduces the latter's ability to enter into condensations; this is borne out by the diminution of the yields of mono- and diphenyl derivatives and the absence of higher polyphenyl derivatives in the end products of reactions effected in the presence of $AlCl_3$-R.

3. A halogen atom attached to the double bond is practically unreactive in the presence of $AlCl_3$.

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# ALKYLATION OF AROMATIC COMPOUNDS IN THE PRESENCE OF ZINC CHLORIDE

## IV. CONDENSATION OF HALOGEN DERIVATIVES AND ALCOHOLS WITH AROMATIC COMPOUNDS UNDER PRESSURE

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In the first paper of this series [1] it was noted that condensation in the presence of zinc chloride can be effected only at fairly high temperatures (150-190°); when low-boiling components are used, the reactions were carried out by gradually adding them to fused $ZnCl_2$ [1,2]. The favorable effect of an excess of HCl upon the course of condensation was likewise established.

In the present paper we made a study of alkylation with $ZnCl_2$ in an autoclave, which enabled us to attain the temperatures required for any components. As has been already noted [1], some old research papers describe the alkylation of benzene by alcohols with $ZnCl_2$ present in sealed tubes at 180-300°; low yields of alkyl benzenes were obtained.

Only a few papers have been devoted to the use of $ZnCl_2$ for the alkylation of halogen derivatives. A comparative study of the activity of $AlCl_3$, $FeCl_3$, and $ZnCl_2$ as catalysts was made in the reactions of allyl chloride with benzene [3]; $FeCl_3$ proved to be best. The condensation of sec.-butyl bromide with 3-methyl-4-chlorophenol in the presence of $ZnCl_2$ has been described [4]. In a recent paper [5] it is stated that $ZnCl_2$ proved to be the best catalyst for the condensation of tert.-butyl chloride with naphthalene and tetralin; the reaction takes place at 90-100° and produces 30-33% of the theoretical yield of butylnaphthalene and butyltetralin. The authors comment on the superiority of $ZnCl_2$ over $AlCl_3$, which yields various by-products. Various patents [6] propose the use of either $ZnCl_2$ or a mixture of it with $AlCl_3$ for condensing aromatic compounds with alkyl halides. There is a much larger number of papers and patents on the alkylation of aromatic compounds by olefins with $ZnCl_2$, Isagulyants and Bagryantseva [7] for example, synthesized butylphenol from phenol and isobutylene, and also synthesized tert.-butyl chloride.

We have made a study of the condensations of n-butyl chloride with benzene, toluene, naphthalene, and phenol; we also carried out some experiments with isoamyl chloride and ethyl bromide.

The reactions were carried out at 170-250° in a steel bomb with an approximate capacity of 100 ml; we used considerable quantities of $ZnCl_2$ (0.5-0.82 mol) to begin with, but we subsequently found that 0.1-0.2 mol per mol of the alkyl halide was adequate, which agreed with our findings for acylation reactions [8].

We obtained approximately 80% of the theoretical yields of the monoalkyl derivatives in our experiments with n-butyl chloride and isoamyl chloride; the yields with naphthalene were somewhat lower (60-70%). Our condensations with ethyl bromide produced only 40-45% of the theoretical yields of the monoalkyl derivatives, together with many high-boiling products.

To ascertain the role of $ZnCl_2$ in these reactions, we made several tests at lower temperatures (100-150°) in ordinary glass apparatus, without pressure. In every case the yields of alkyl derivatives were very low; this led us to conclude that the mechanism of condensation with $ZnCl_2$ differs from that with $AlCl_3$. Apparently, high temperatures are required for the formation of active intermediate compounds (possibly olefins). Endeavors to effect condensation by heating n-butyl chloride with toluene to 260° in a bomb without adding any $ZnCl_2$ failed to yield even a trace of alkyl benzenes. The catalytic role of $ZnCl_2$ at high temperatures and pressure is therefore obvious.

We then studied the condensation of n-butyl, isopropyl, and ethyl alcohols with benzene and toluene under pressure. These experiments were carried out by heating the alcohol, saturated with hydrogen chloride, in a bomb together with benzene (or toluene) and $ZnCl_2$. When ethyl alcohol is used, a temperature of approximately 300° is required for the reaction to proceed; the yields of ethylbenzene are low, and many polyalkyl benzenes are formed. With the two other alcohols the condensations take place readily at 220-230°, and the yields of monoalkyl benzenes (75-80% of the theoretical) are higher than in the same reactions without pressure (50-70%) [1]. In these experiments we also found that the amount of $ZnCl_2$ used could be extremely small: 0.1 mol and even 0.02 mol per mol of alcohol, for instance, produce approximately 75% of the theoretical yield of butyl toluene. Our efforts to effect condensation without adding any $ZnCl_2$ at all, by heating a mixture of the alcohol saturated with HCl and toluene to 250° in a bomb for a long time yielded negative results.

It should be noted that condensations of n-butyl alcohol with toluene in the presence of $AlCl_3$ yield poor results owing to cleavage of the alcohol [9]. Analysis of the condensation products of benzene with n-butyl alcohol and n-butyl chloride by synthesizing their acetamino derivatives [10] showed that secondary butylbenzene was formed; this isomerization of the radical bears out the hypothesis that olefins are formed as intermediate products in these condensations.

## EXPERIMENTAL

An acidproof steel bomb, encased in an iron housing with a pocket for a thermometer, was heated with a Bunsen burner. The reaction lasted 8-12 hours. The reaction mixture was decomposed by acidulated water and then distilled with steam. The hydrocarbon mixture recovered was desiccated and fractionated.

In this reaction we used freshly fused $ZnCl_2$ with HCl added; the spent $ZnCl_2$ is easily regenerated.

1. Benzene – n-butyl chloride. Taken: 18 ml $C_6H_6$; 9.2 g (0.1 mol) n-$C_4H_9Cl$; and 2.5 g (0.018 mol) $ZnCl_2$. The mixture was heated to 225-230° for 10 hours. This yielded: 9.5 g (70 % of the theoretical) of butylbenzene (b.p. 167-173° at 722 mm) and 1.5 g (8%) of dibutylbenzene (b.p. 235-240°).

Fractionation of the crude butylbenzene yielded sec.-butylbenzene with a b.p. of 171-173° (722 mm).

$d_{25}^{20}$ 0.8628; $n_D^{20}$ 1.4920; $MR_D$ 45.59; computed $MR_D$ 45.70.

0.0846 g substance: 0.2772 g $CO_2$; 0.0786 g $H_2O$.

Found %: C 89.36; H 10.39.

$C_{10}H_{14}$. Computed %: C 89.55; H 10.45.

The acetamino derivative had a m.p. of 124-125°; the other fractions of the crude butylbenzene yielded a derivative with a m.p. of 122-123°. A test sample mixed with some of the acetamino derivative prepared by T.E.Zalesskaya [11] that we had exhibited no depression of the melting point.

2. Benzene – isoamyl chloride. Taken: 18 ml $C_6H_6$; 4 g (0.04 mol) iso-$C_5H_{11}Cl$; and 2 g (0.015 mol) $ZnCl_2$. The mixture was heated to 230-240° for 10 hours. This yielded: 3.5 g (64% of the theoretical) of amylbenzene and 1.2 g of polyalkyl benzenes. We recovered:

Tert.-amylbenzene. B.p. (725 mm) 185-190°; $d_{28}^{28}$ 0.8683; $n_D^{20}$ 1.4912. $MR_D$ 49.32; computed $MR_D$ 49.39.

3. Toluene – n-butylchloride. Taken: 20 ml $C_7H_8$; 9.2 g (0.1 mol) n-$C_4H_9Cl$; and 1.5 g (0.011 mol) $ZnCl_2$. The mixture was heated to 210-220° for 8 hours. This yielded: 10.5 g (71% of the theoretical) of sec.-butyltoluene and 2.5 g of polyalkyl benzenes (b.p. 240-245°). We recovered:

Sec.-butyltoluene (a mixture of isomers): B.p. 191-195° (723 mm); $d_{28}^{28}$ 0.8640; $n_D^{20}$ 1.4935.

0.1800 g substance: 0.5890 g $CO_2$; 0.1748 g $H_2O$.
Found %: C 89.25; H 10.75.
$C_{11}H_{16}$. Computed %: C 89.19; H 10.81.

4. Naphthalene – n-butyl chloride. Taken: 12.8 g $C_{10}H_8$; 9.2 g (0.1 mol) n-$C_4H_9Cl$; and 4 g (0.03 mol) $ZnCl_2$. The mixture was heated to 160-170° for 12 hours. This yielded: 12 g (65% of the theoretical) of butylnaphthalene and 2.2 g (9% of the theoretical) of dibutylnaphthalene.

Butylnaphthalene (undetermined structure): b.p. 278-283° (722 mm); 156-160° (15 mm); $d_{28}^{28}$ 0.9798; $n_D^{20}$ 1.5700.

Dibutylnaphthalene. B.p. 170-180° (15 mm); $n_D^{20}$ 1.5807; $d_{28}^{28}$ 0.9682.

5. Phenol – n-butyl chloride. Taken: 19 g (0.22 mol) $C_6H_5OH$; 14 g (0.15 mol) n-$C_4H_9Cl$, and 4 g (0.03 mol) $ZnCl_2$. The mixture was heated to 170-180° for 7 hours.

After decomposition with acidulated water, the mixture was extracted with ether; the ether extract was repeatedly treated with 5% NaOH to extract the phenols. The alkaline solution was acidulated and extracted with ether.

This yielded: 16 g (72% of the theoretical) of butylphenols and 4 g (12%) of butyl phenylate (b.p. 245-250° at 725 mm, $n_D^{20}$ 1.5090). Fractionation of the crude butylphenol yielded two isomers.

I. Sec. butylphenol. B.p. 230-235° (720 mm); $d_{28}^{28}$ 0.9890; $n_D^{20}$ 1.5178.
0.1640 g substance: 0.4790 g $CO_2$; 0.1422 g $H_2O$.
Found %: C 79.61; H 9.60.
$C_{10}H_{14}O$. Computed %: C 80.00; H 9.33.

II. Sec.-butylphenol (para) B.p. 242-246° (725 mm); $d_{28}^{28}$ 0.9860; $n_D^{20}$ 1.5185.

6. Toluene – ethyl bromide. Taken: 15 ml $C_7H_8$; 11 g (0.1 mol) $C_2H_5Br$; and 7 g (0.05 mol) $ZnCl_2$. The mixture was heated to 230-240° for 14 hours. This yielded: 3.7 g (30% of the theoretical) of ethyltoluenes (b.p. 156-165°; $n_D^{20}$ 1.4980) and 2 g of polyalkyl benzenes (b.p. 190-198°).

7. Benzene – n-butyl alcohol. Taken: 20 ml $C_6H_6$; 7.4 g (0.1 mol) n-$C_4H_9OH$; and 3.4 g (0.025 mol) $ZnCl_2$. The alcohol was saturated with anhydrous HCl at 0°

(added weight 3.5 g). The mixture was heated to 235-240° for 12 hours. This yielded 9 g (67% of the theoretical) of butylbenzene and 1.8 g (10%) of dibutylbenzene (b.p. 235-240°).

Sec.-butylbenzene: B.p. 170-173° (722 mm); $d_{28}^{28}$ 0.8620; $n_D^{20}$ 1.4940; acetamino derivative: m.p. 123-124°.

8. Toluene - n-butyl alcohol. Taken: 20 ml $C_7H_8$; 7.4 g n-butyl alcohol (saturated with HCl; added weight 3.5 g); and 13.6 g (0.1 mol) $ZnCl_2$. This yielded: 11 g (74% of the theoretical) of butyltoluene (b.p. 192-195°; $d_{28}^{28}$ 0.8625; $n_D^{20}$ 1.4908); and 1 g (5%) of dibutyltoluene (b.p. 240-245°; $n_D^{20}$ 1.4920).

Similar condensations were carried out with 3.4 g (0.025 mol) and 1.5 g (0.011 mol) of $ZnCl_2$; the respective yields of butyltoluene were 10.6 g (71.5% of the theoretical) and 7.5 g (51% of the theoretical).

9. Benzene - ethylalcohol. Taken: 10 ml $C_6H_6$; 4.6 g (0.1 mol) $C_2H_5OH$ saturated with HCl; and 3.4 g $ZnCl_2$. The mixture was heated to 330-340° for 12 hours. This yielded: 3.4 g (36% of the theoretical) of ethylbenzene and 4 g of polyalkyl benzenes (b.p. 150-180°).

The same results were obtained by heating the mixture to 280-290° with 13.6 g (0.1 mol) of $ZnCl_2$.

10. Benzene - isopropyl alcohol. Taken: 20 ml $C_6H_6$; 6 g (0.1 mol) iso-$C_3H_7OH$ saturated with HCl; and 6.8 g (0.05 mol) $ZnCl_2$. The mixture was heated to 210-220° for 10 hours.. This yielded: 9 g (75% of the theoretical) of isopropylbenzene and 2.5 g (15% of the theoretical) of diisopropylbenzene.

Isopropylbenzene. B.p. 150-153° (720 mm); $d_{28}^{28}$ 0.8751; $n_D^{20}$ 1.4895.
0.1200 g substance: 0.3920 g $CO_2$; 0.1104 g $H_2O$
Found %: C 90.50; H 9.50.
$C_9H_{12}$. Computed %: C 90.00; H 10.00.

## SUMMARY

1. It has been shown that aromatic compounds can be alkylated by alkyl halides in the presence of $ZnCl_2$ when the reaction is carried out under pressure at 180-230°.

2. A study has been made of the alkylation of aromatic compounds by alcohols saturated with HCl, in the presence of $ZnCl_2$ and under pressure. It has been shown that under these conditions the yields of alkyl derivatives are higher than when these reactions are carried out not under pressure.

3. It has been established that if the temperature is high enough, the amount of $ZnCl_2$ required for the reaction may be as low as 0.1-0.2 mol per mol of the alkylating reagent.

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# RESEARCHES ON THE DERIVATIVES OF QUINOLINE

## VI. JOINT CONDENSATION OF AROMATIC AMINES, 1,2-PROPYLENE GLYCOL, AND ACETONE*

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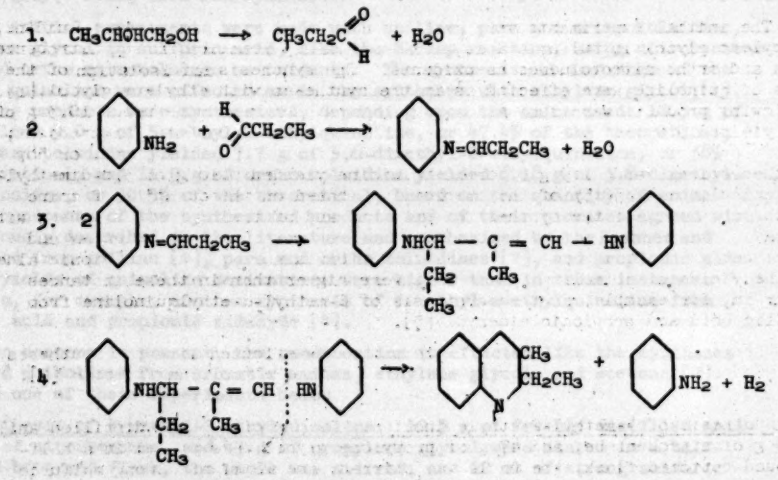
In our previous reports we described a method of preparing quinoline derivatives from aromatic amines and ethylene glycol [1], as well as when ketones participate in the condensation [2].

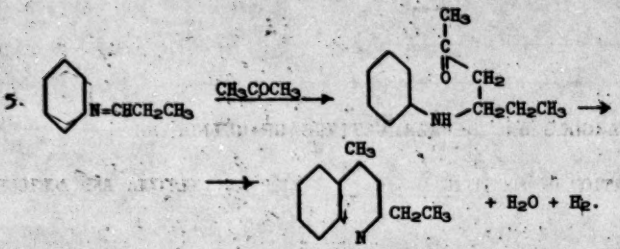
Desiring to apply this method to other alpha glycols, we have used it in the present paper for the synthesis of alkylated quinolines, substituting propylene glycol for the ethylene glycol. In accordance with the previously elaborated mechanism for syntheses with ethylene glycol [2,3], we consider the principal condensation reactions to be the formation of propylidene derivatives of aryl amines, the formation of Eibner and Eckstein bases from the latter, and their subsequent transformations.

For aniline, say, the following diagram may be held to apply:



*Cf Report V in J. Gen. Chem. 19, 1656 (1949), (CB translation pp 485 ff.

When acetone is present:



It should be noted that in syntheses with acetone present the product yields are somewhat higher than was found when ethylene glycol was used. This is apparently due to the fact that cyclization is easier to accomplish when acetone is present. The lesser tarring and the higher product yields enable us to observe this pattern of behavior, which cannot be noticed in syntheses with ethylene glycol owing to the greater extent of tarring. This behavior pattern is especially striking in reactions with diamines, as we shall illustrate in our next report. The alkylated quinolines synthesized for the first time may be employed in the preparation of cyanin and quinophthalone dyes and may also serve as standards in analyzing the quinoline bases in coal tar and petroleum.

## EXPERIMENTAL

The propylene glycol was prepared from glycerol by heating the latter with powdered caustic soda, [4]. As it contains various impurities when prepared by this method: such as lactic, propionic, oxalic, and formic acids, propyl and allyl alcohols, etc. [5], it was redistilled twice, a freshly distilled preparation with a b.p. of 188-190° being used for synthesis.

The initial experiments were made with aniline, para and ortho toluidine, and propylene glycol in sulfuric acid, like the Skraup reaction, using nitrobenzene and para and ortho nitrotoluenes as oxidants. The synthesis and isolation of the homologs of quinoline were effected as in the syntheses with ethylene glycol, [1]. The following products were synthesized, depending upon the amine used: 10.3 g of aniline yielded 9.0 g of 3-methyl-2-ethylquinoline, or 47.4% of the theoretical; 11.9 g of para toluidine yielded 7.7 g of 3,6-dimethyl-2-ethylquinoline, or 38% of the theoretical; and 11.9 g of ortho toluidine yielded 6.18 g of 3,8-dimethyl--2-ethylquinoline, or 30.5% of the theoretical, based on the quantity of amine used. The constants of the synthesized products and of their picrates agreed with those previously described in the literature and synthesized by the Doebner and Miller method from aniline [6], para and ortho toluidines [7], and propionic aldehyde. The yields of quinoline derivatives were higher than in these instances [6,7] or in, for example, another synthesis of β-methyl-α-ethylquinoline from anthranilic acid and propionic aldehyde [8].

When acetone is present, the condensation is effected like the syntheses of alkylated quinolines from aromatic amines, ethylene glycol, and acetone [2]. We describe one of these experiments below.

Synthesis of 4-methyl-2-ethylquinoline. 10.3 g of freshly distilled aniline, 7.0 g of nitrobenzene, and 47 g of propylene glycol were placed in a half-liter round-bottomed flask, the whole was stirred, and 22 ml of strong sulfuric

acid was added. After careful stirring, the flask was connected to a reflux condenser through which 14 ml of acetone was added drop by drop, while the mixture was gently heated over an oil bath.

The mixture was then heated to a gentle boil (this took place at 140-145°), first for 10 hours, after which the water was driven off for 2 hours, passing over together with the unreacted acetone and some of the nitrobenzene, the total amount being 15-18 ml. After the water had been driven out of the flask, 7 ml of acetone was added and the mixture was heated for another 7 hours. The mixture was then cooled to room temperature and diluted with water, and the unreacted nitrobenzene was driven off with steam. The residue was alkalinized with a 40% solution of sodium hydroxide, and the bases were driven off with steam. The distillate was acidulated with 15 ml of strong sulfuric acid until all the sulfates of the bases had dissolved, cooled to room temperature and diazotized to eliminate the aniline by pouring in 5 g of sodium nitrite dissolved in 25 ml of water. The reaction mixture was heated over a water bath until no more nitrogen was evolved and again acidulated; the quinoline base was then driven off with steam. The distillate was extracted with ether and desiccated with potash, the ether was driven off, and the 2-ethyl-4-methylquinoline was distilled from a Wurtz flask. The yield of a product with a b.p. of 270-275° was 9.6 g, or 50.1% of the theoretical.

4-Methyl-2-ethylquinoline is a light-yellow oily liquid with the characteristic odor of a quinoline base, resembling that of quinaldine; it is readily soluble in alcohol, ether, benzene, chloroform, and acetone. Its refractive index is $n_D^{20}$ 1.5941 and its density $d_{20}^{20}$ 1.027. The picrate, precipitated from an alcoholic solution of the base by a saturated alcoholic solution of picric acid, is a finely crystalline yellow powder with a m.p. of 159°.

0.1065 g substance: 13 ml $N_2$ (19°, 758 mm).
Found %: N 14.23.
$C_{12}H_{13}N \cdot C_6H_2OH(NO_2)_3$. Computed %: N 14.0.

When a solution of platinic chloride in hydrochloric acid is added to a hydrochloric solution of the base, a double salt precipitates out. It crystallizes from boiling dilute hydrochloric acid as fine dark-yellow crystals. For analysis, the salt was successively washed with water, alcohol, and ether. M.p. 219°. It contains no water of crystallization.

0.2679 g substance: 0.0687 g Pt.
Found %: Pt 25.64.
$(C_{12}H_{13}NHCl)_2PtCl_4$ Computed %: Pt 25.95.

The double salt with palladium chloride $(C_{12}H_{13}NHCl)_2PdCl_2$, precipitated from a hydrochloric solution, is a finely crystalline brick-red powder with a m.p. of 249°.

The quinophthalone base is a brown powder that does not melt up to 360°. When sulfurated with 25% oleum and isolated, as usual, as sodium salts of sulfo acids, it is a brown powder that is readily soluble in water, giving the latter a yellow tint. It dyes wool and silk light-brown.

Synthesis of 4,6-dimethyl-2-ethylquinoline. 4,6-Dimethyl-2-ethylquinoline was synthesized, like 4-methyl-2-ethylquinoline, from para toluidine, propylene glycol, and acetone in sulfuric acid, using para nitrotoluene as an oxidant. 11.9 g of para toluidine yielded 8.7 g of a product with a b.p. of 285-290°, or 42.3% of the theoretical yield. A light-yellow, oily liquid with an odor close to that of quinaldine, which dissolves easily in organic solvents. Its refractive index is $n_D^{20}$ 1.5889 and its density $d_{20}^{20}$ 1.0236. The picrate, precipitated from an alcoholic

solution, has a m.p. of 193°.

0.1000 g substance: 12.4 ml $N_2$ (20°, 752 mm).
Found %: N 13.83.
$C_{13}H_{15}N \cdot C_6H_2OH(NO_2)_3$. Computed %: N 13.53.

The double salt with platinic chloride is dark yellow and contains no water of crystallization. M.p. 203°.

0.2243 g substance: 0.0556 g Pt.
Found %: Pt 24.79.
$(C_{13}H_{15}NHCl)_2PtCl_4$. Computed %: Pt 25.02.

Synthesis of 4,8-dimethyl-2-ethylquinoline. This synthesis was performed with ortho toluidine, propylene glycol, and acetone, ortho nitrotoluene being employed as an oxidant. 11.9 g of ortho toluidine yielded 7.3 g of a product with a b.p. of 275-280°, or 35.7% of the theoretical. A light-yellow, oily liquid with a characteristic odor, which is soluble in organic solvents. Its refractive index is $n_D^{20}$ 1.5849 and its density $d_{20}^{20}$ 1.0011. The picrate, precipitated from an alcoholic solution, has a m.p. of 147°.

0.115 g substance: 13.7 ml $N_2$ (23°, 762 mm).
Found %: N 13.77.
$C_{13}H_{15}N \cdot C_6H_2OH(NO_2)_3$. Computed %: N 13.53.

The double salt with platinic chloride is dark yellow and contains no water of crystallization. M.p. 217°.

0.3280 g substance: 0.0820 g Pt.
Found %: Pt 25.0.
$(C_{13}H_{15}NHCl)_2PtCl_4$. Computed %: Pt 25.02.

The student T.P.Ilyina took part in this research.

## SUMMARY

1. 3-Methyl-2-ethylquinoline, 3,6-dimethyl-2-ethylquinoline, and 3,8-dimethyl-2-ethylquinoline have been synthesized from aniline, ortho and para toluidine, and 1,2-propylene glycol in sulfuric acid, in a Skraup reaction, with better yields than are attainable by the well-known Doebner-Miller method, using aromatic amines and propionic aldehyde.

2. 4-Methyl-2-ethylquinoline, 4,6-dimethyl-2-ethylquinoline, and 4,8-dimethyl-2-ethylquinoline, not previously described in the literature, have been synthesized from aniline, ortho and para toluidine, 1,2-propylene glycol, and acetone in sulfuric acid, with higher yields than in syntheses in which no acetone is present.

3. The synthesis of alkylated quinolines from aromatic amines and ethylene glycol, as well as with ketones taking part, has been applied to propylene glycol and apparently is a general reaction, i.e, it is applicable to other primary-secondary α-glycols.

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# THE REACTIONS OF α,β-UNSATURATED ALDEHYDES WITH AROMATIC AMINES

## III. DIPHENYLAMINEACROLEIN*

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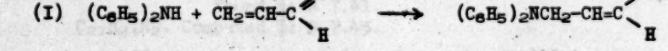
Little research has been done on the reaction of α,β-unsaturated aldehydes with secondary aromatic amines. It has been said that no reaction takes place under ordinary conditions; G. E. Rudchenko came to this conclusion with respect to diphenylamine, for example, in his research on the reaction of furylacrolein with various amines [1].

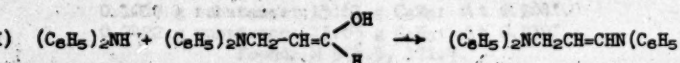
Leeds, who was the first to synthesize diphenylamineacrolein [2], describes it as an infusible, amorphous substance with the empirical formula $C_{27}H_{24}N_2$. He conjectured that this compound is allylidene-bis-diphenylamine $CH_2=CH-CH=[N(C_6H_5)_2]_2$; this is the name given for it in Beilstein's handbook as well [3]. In his paper, Leeds gives the analysis of the synthesized product, but he does not give the molecular weight of the substance, which would have been quite desirable, inasmuch as it would have been natural to assume that the infusible substance he had isolated was a polymerized product.

In our research we found that diphenylamineacrolein is a crystalline substance with a m.p. of 145°. There is reason to believe that it has the structure of 1,3-bisdiphenylaminopropene, i.e., that the reaction is similar to the reaction of α,β- unsaturated aldehydes with secondary amines, which has been studied in detail, [4].

The diene structure of acrolein (1,4 addition) is reflected in the mechanism of the reaction:



(I) $(C_6H_5)_2NH + CH_2=CH-C(=O)H \longrightarrow (C_6H_5)_2NCH_2-CH=C(OH)H$



(II) $(C_6H_5)_2NH + (C_6H_5)_2NCH_2-CH=C(OH)H \longrightarrow (C_6H_5)_2NCH_2CH=CHN(C_6H_5)_2 + H_2O$,

i.e., we get a compound with the structure of an Eibner and Eckstein base [5].

Hence, as we see it, the product of the reaction of diphenylamine with acrolein is a member of an as yet unknown series of tertiary aliphatic-aromatic

* Cf. J. Gen. Chem. 16, 1, 47-54 (1946) for Reports I and II.

amines. The simple method evolved by us for synthesizing it also makes other members of this series accessible.

## EXPERIMENTAL*

The acrolein was prepared from glycerol, sulfuric acid, and $KHSO_4$ [6]. The diphenylamine was chemically pure, with a m.p. of 56°.

The initial tests were made according to Leed's prescription: heating an alcoholic solution of diphenylamine with acrolein to 40-45° for 12 hours over a water bath. The ensuing treatment with boiling water and alcohol, successively, produced a negligible yield (5-10%) of a compound with a m.p. ranging from 106 to 118°, contrary to Leed's description. When heating was continued for more than 18 hours, the reaction mixture turned red, apparently because of the formation of oxidation products. When a drop of hydrochloric acid is added, the reaction is energetic, polymerization products being formed. The acrolein and diphenylamine must be taken in equivalent proportions or, even better, using a slight excess of acrolein — if this is not done, the reaction will not proceed as indicated. After several experiments performed in flasks and sealed tubes, we worked out the following method for synthesizing diphenylamineacrolein.

### Synthesis of Diphenylamineacrolein

60 g of diphenylamine and 25 ml of acrolein were placed in a half-liter round-bottom flask, and the flask was closed with a solid rubber stopper, which was fastened with wire and cemented on top with lead putty ($Pb_2O_3$ and glycerol). The mixture was heated for 8-10 hours over a boiling water bath, and then it was allowed to stand for 4 hours on ice. After standing on ice, the initially pale-yellow syrupy solution was transformed into a dense mass of crystals that resembled old, candied honey. The mixture was then treated with alcohol. As soon as the alcohol began to boil, a white crystalline precipitate was thrown down; this was filtered out and desiccated for 3 to 4 hours. The product yield was 45 g, or 33.7% of the theoretical, based on the diphenylamine. Some more of the product (10-13 g) could be recovered from the mother liquor. Diphenylamineacrolein is readily soluble in ether, benzene, acetone, chloroform, and ethyl acetate, less so in petroleum ether, poorly soluble in alcohol, and hardly soluble at all in cyclohexane. It dissolves more easily in boiling alcohol, crystallizing as true parallelepipeds. It is hydrolyzed in dilute hydrochloric acid, the odor of acrolein being perceptible. The melting point of pure diphenylamineacrolein is 145°. A solution of diphenylamineacrolein in sulfuric acid is cherry-red.

0.2299 g substance: 0.7274 g $CO_2$; 0.1339 g $H_2O$.
Found %: C 86.29; H 6.41.
$C_{27}H_{24}N_2$. Computed %: C 86.17; H 6.38.

0.2718 g substance: 17.05 ml $N_2$ (16°, 760 mm).
Found %: N 7.41.
$C_{27}H_{24}N_2$. Computed %: N 7.45.

0.1067 g substance: 13.63 g $C_6H_6$: $\Delta t$ 0.104°.
0.2422 g substance: 13.63 g $C_6H_6$: $\Delta t$ 0.239°.
Found: M 376.3, 371.7.
$C_{27}H_{24}N_2$. Computed: M 376.

When distilled in vacuum (20 mm) up to 270°, diphenylaminoacrolein breaks down, yielding diphenylamine. 5 g of the substance yielded 1.5 g of diphenylamine and a tarry residue in the distilling flask. After distillation was stopped, the

* Performed in the organic chemistry laboratory of the Sverdlovsk Polytechnic Institute.

sharp odor of acrolein was noticed in the flask. It may be assumed that, as in the thermal decomposition of bases synthesized from secondary aliphatic amines and α,β-unsaturated aldehydes [4], one molecule of diphenylamine is detached during distillation and diphenylamineallene is formed, which polymerizes to a tar. With this mechanism of the hydrolytic and thermal decomposition of the enamines we understand why secondary aromatic amines do not form quinoline derivatives when heated with unsaturated aldehydes, or in the Skraup or Doebner-Miller reactions.

## SUMMARY

1. It has been established that the product of the reaction between acrolein and diphenylamine is not that described by Leeds.

2. Diphenylamineacrolein is a crystalline product with a m.p. of 145°, which apparently has the structure of 1,3-bis-diphenylaminopropene.

3. The method developed for the synthesis of diphenylamineacrolein may be used to synthesize other members of the series of tertiary aliphatic-aromatic amines.

4. The mechanism of the hydrolytic and thermal decomposition of diphenylamineacrolein justifies the conclusion that it is impossible to synthesize quinoline derivatives from secondary aromatic amines in the Skraup or Doebner-Miller reactions.

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# SYNTHESIS OF MONOCHLOROPHTHALIC ANHYDRIDES FROM MONONITROPHTHALIC ANHYDRIDES

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Though phthalic anhydride is one of the most important products of basic organic synthesis [1] and is widely employed [2,3], its substituted products, particularly the monochloroanhydrides, are rarely encountered even in laboratory practice. In view of the undoubted interest attached to these compounds [4], this state of affairs can be due solely to the difficulties of obtaining these substances in the pure state.

Theoretically, two monochlorophthalic anhydrides are possible: the 3-chlorophthalic and the 4-chlorophthalic. These anhydrides or their acids have been synthesized in various ways.

3-Chlorophthalic acid. This was synthesized by Bogert and Boroschek [5] by reacting $PCl_5$ with 3-nitrophthalic anhydride. The acid was also synthesized by oxidizing 3-chloro-2-methylbenzoic acid, 1,5-dichloronaphthalene, and α-chlorotetralin. In a British patent [6] the acid anhydride was synthesized by chlorinating 3-nitrophthalic anhydride; in the U.S. patent phthalic anhydride was chlorinated to produce it. Neither patent indicates the requisite conditions for obtaining pure 3-chlorophthalic acid or its anhydride.

4-Chlorophthalic acid. The more numerous methods of synthesizing 4-chlorophthalic acid may be classified into three groups according to the initial materials used. Auerbach [7] synthesized 4-chlorophthalic acid by chlorinating an alkaline solution of phthalic acid. Ruchinsky [8] and other authors synthesized the acid by changing the alkali and the proportions used. A patent was issued in 1929 covering the synthesis of 4-chlorophthalic acid by chlorinating phthalic acid in a solution of caustic alkalies, and sodium and potassium carbonates, bicarbonates, and acetates.

The second group comprises methods of synthesizing the acid by oxidizing the products of chlorinating naphthalene and its derivatives, as well as some other aromatic compounds containing chlorine. Thus, the acid was synthesized by oxidizing 1,6-, 2,6-, and 2,7-dichloronaphthalenes, 6-chloronaphthol-2, β-chlorotetralin, 4-chloro-2-methylbenzoic acid, 1-methyl-3-chloro-6-acetylbenzene, and 6-chlorohydrindone.

The third group comprises the methods of synthesizing the acid or its anhydride from derivatives of phthalic acid or its anhydride by substituting chlorine for some of the functional groups in position 4. The acid or its anhydride was synthesized from the trichloride of 4-sulfophthalic acid and $PCl_5$, 4-sulfophthalic

anhydride and $NaClO_3$, 4-nitrophthalic acid via the diazo compound of diethyl 4-aminophthalate, and (according to a patent) by chlorinating 4-nitrophthalic anhydride.

Most of the foregoing methods of synthesizing monophthalic acids or their anhydrides are inconvenient, owing to the inaccessibility of the initial materials or else the difficulties encountered in purifying the end products. A study of the literature indicates that the Bogert and Boroschek method [5] is most often employed to synthesize 3-chlorophthalic acid, and that phthalic acid is usually chlorinated in an alkaline solution to synthesize 4-chlorophthalic acid. In the latter instance, difficulties are encountered in purifying the 4-chlorophthalic acid from the traces of phthalic and 4,5-dichlorophthalic acids.

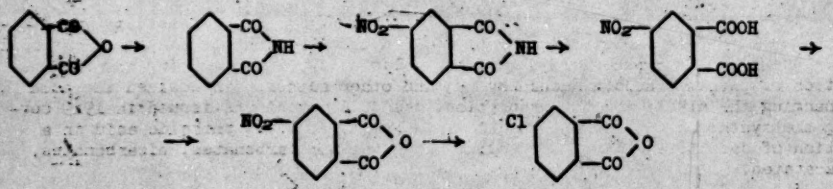
As we had to have 3- and 4-chlorophthalic acids, preferably in the form of their anhydrides, we turned our attention to synthesizing the latter from the respective nitro derivatives in accordance with the British patent [6]. This method attracted our attention because of the well-developed methods for preparing the initial materials: 3-nitrophthalic and 4-nitrophthalic anhydrides. Moreover, replacement of the nitro group by elementary chlorine was also of considerable interest from the standpoint of the development of the methods of organic chemistry. This latter problem will be the subject of a separate paper.

Owing to the fact that the patent gave but few details, we decided to make a series of investigations to work up a method for the synthesis of these anhydrides.

The monochlorophthalic anhydrides were synthesized in accordance with the following diagram:

3-Chlorophthalic Anhydride

4-Chlorophthalic anhydride



## EXPERIMENTAL

The initial material for the synthesis of monochlorophthalic anhydrides was commercial phthalic acid, produced by the disintegration of domestic commercial phthalic anhydride during storage. The melting point of the acid in a sealed capillary was 183-190°. In view of the fact that the monochlorophthalic anhydrides synthesized from commercial phthalic anhydride and the intermediate products are often used without further purification, and also in order to ascertain the yield of inter-

mediate and end products, it is desirable to give a brief description at this point of the entire synthesis, beginning with the phthalic anhydride.

Phthalic anhydride. This was prepared from the acid by heating the latter in a wide-necked flask over an asbestos screen to 200-260° until no more steam was evolved.

3-Nitrophthalic acid. This was prepared by nitrating phthalic anhydride with nitric acid. 250 g of commercial phthalic anhydride yielded, after purification, 92 g of 3-chlorophthalic acid with a melting point of 221-223° in a sealed capillary.

3-Nitrophthalic anhydride. 25 g of 3-nitrophthalic acid was placed in a wide-mouthed, short-necked 50 ml flask, and heated to 190-250° for 15-20 minutes over a sand bath. The melting point of the end product was 160-170°. The yield was 22.2-22.7 g.

3-Chlorophthalic anhydride. 22 g of 3-nitrophthalic anhydride was placed in a wide test tube fitted with a stopper and inlet and outlet tubes. The test tube was immersed in a paraffin bath and kept at a temperature of 230-250° while a slow current of desiccated chlorine was passed through it. The sublimate formed during chlorination was scraped off to the bottom of the test tube at intervals. After no more brown fumes were evolved, the chlorine was passed through the test tube for another 30-40 minutes, and the process was stopped. Chlorination was complete within 6-7 hours. The yield of a product with a m.p. of 105-109° was 19-20 g. Recrystallization from a 1:1 benzene-gasoline mixture yielded 15-15.5 g of 3-chlorophthalic anhydride with a m.p. of 125.5°. About two more grams of contaminated anhydride may be recovered from the mother liquor. If chlorination should be long drawn out, it is advisable to distill the product from a retort and then to recrystallize it from the benzene-gasoline mixture in order to obtain pure 3-chlorophthalic anhydride.

Phthalimide. 200 g of phthalic anhydride was placed in a round-bottomed flask fitted with an air-cooled reflux condenser, 15% ammonia was added, and the temperature of the mixture was slowly raised to 300°. This yielded a dark-colored phthalimide with a m.p. of 232-234°. The yield was 188 g.

4-Nitrophthalimide. 200 g of phthalimide was nitrated, without further purification, by a mixture of nitric and sulfuric acids. The synthesized 4-nitrophthalimide, which was pale yellow after purification, had a m.p. of 197-198°. The yield was 170 g.

4-Nitrophthalic acid. This was prepared by saponifying 4-nitrophthalimide. Treatment of 80 g of the imide yielded 82 g of 4-nitrophthalic acid with a m.p. of 164.5-167.5°.

4-Nitrophthalic anhydride. This was prepared by the method used to synthesize the 3-nitrophthalic anhydride. 20 g of the acid yielded 17.6 g of the anhydride.

4-Chlorophthalic anhydride. 17 g of 4-nitrophthalic anhydride was chlorinated by the method outlined above. The evolution of brown fumes ceased after 4 hours, and the chlorine was then passed through for another 30-40 minutes, after which the process was stopped. The synthesized product had a melting point of approximately 90°; it was transferred to a retort and distilled at ordinary pressure. Repeated recrystallization from a benzene-gasoline mixture yielded a white crystalline product with a m.p. of 98°. The yield was 10.2 g.

## SUMMARY

1. 3- and 4-Nitrophthalic anhydrides have been synthesized from phthalic acid via a number of intermediate products.

2. Chlorination of the fused 3- and 4-nitrophthalic anhydrides produced good yields of 3- and 4-chlorophthalic anhydrides with m.p. of 125.5 and 98°, respectively.

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# HYDROCARBONS OF THE CYCLOPENTANE SERIES WITH A DOUBLE BOND IN THE SIDE CHAIN

## II. VINYLCYCLOPENTANE

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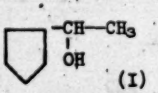
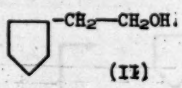
The number of known cyclopentane hydrocarbons with a double bond in the side chain is extremely small [1]. Even the simplest representative of this series – vinylcyclopentane – has been unknown up to the present time; the analogous hydrocarbon of the cyclohexane series – vinylcyclohexane – has been synthesized by Levina [2].

Hypothetically, the synthesis of vinylcyclopentane might start out with α-cyclopentylethanol (I) or β-cyclopentanyl ethanol (II):

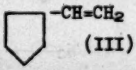


(I)

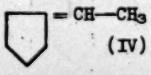


(II)

But the dehydration of cyclopentylethanol might be expected to result in the formation of ethylidenecyclopentane (IV), together with vinylcyclopentane (III):

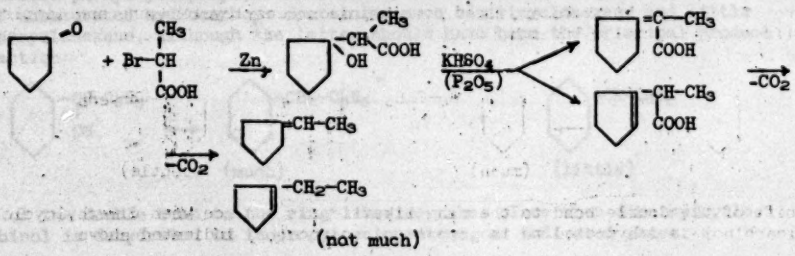


(III)



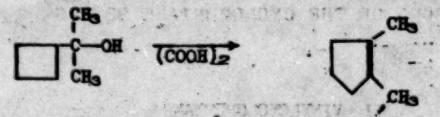
(IV)

Ethylidenecyclopentane has been synthesized by Wallach [3] by condensing cyclopentanone with α-bromopropionic acid, followed by dehydrating the hydroxy acid and decarboxylating the synthesized cyclopentylidenepropionic acid:



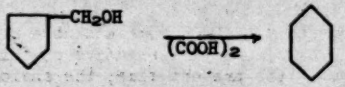
(not much)

Moreover, dehydration of cyclopentane alcohols possessing a hydroxyl group in the side chain may also result in isomerization of the ring. When dehydrating dimethylcyclobutylcarbinol with oxalic acid, Kinzher [4] observed the formation of 1,2-dimethylcyclopentene:

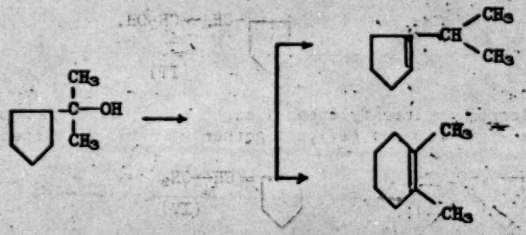


Reacting hydrohalic acids with cyclopentylcarbinol, Nametkin and Morozova [5] synthesized a halogen derivative of cyclohexane:

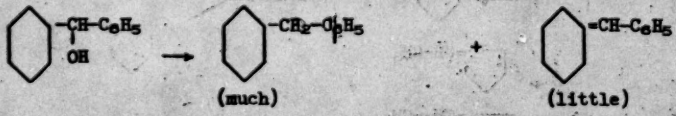
Dehydrating the same cyclopentylcarbinol, Rozanov [6] obtained cyclohexene:



Kazansky and Tatevosyan [7] dehydrated dimethylcyclopentylcarbinol with oxalic acid and obtained the normal reaction product, 1-isopropylcyclopentene-1; but Nametkin and Gabriadze [8] made a more detailed study of this reaction and showed that, in addition to the normal reaction product, dimethylcyclohexene is also formed, i.e., dimethylcyclopentylcarbinol behaves like Kinzher's diemthylcyclobutylcarbinol:



In addition to ring isomerization, dehydration may also result in migration of the double bond from the side chain to the ring; Auwers and Treppman, for instance, [9], dehydrated phenylcyclohexylcarbinol with potassium bisulfate and obtained a mixture of unsaturated hydrocarbons containing much benzylcyclohexene and little benzylidenecyclohexane, although the latter should have been the principal product of the reaction:




The shift of the double bond to the ring likewise takes place when dimethylcyclopentylcarbinol is dehydrated to isopropylcyclopentene, as indicated above.

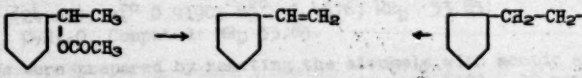
One of the most dependable methods of dehydrating alcohols is Chugayev's xanthogenate method, by means of which dimethylcyclobutylcarbinol can be dehydrated without isomerizing the ring, as Kazansky [10] has shown; Kazansky obtained a mixture of isopropylidenecyclobutane and asymm. methylcyclobutylethylene:

D.N.Kursanov [11] used the same method to synthesize benzylidenecyclohexane from cyclohexylphenylcarbinol.

We chose a different method of synthesis, viz: the Wibaut and Van Pelt pyrolysis of acetates [12]. This method has been extensively employed in recent years in the synthesis of olefins with the assigned position of the double bond.

An unsuccessful endeavor to convert α-cyclopentylethanol into an unsaturated hydrocarbon is described in the literature. Venus-Danilova and Bolshukin [13] dehydrated this alcohol with sulfuric acid of different concentrations, potassium bisulfate, and anhydrous oxalic acid, but in all their experiments the α-cyclopentylethanol was recovered unchanged, together with a small quantity of tarring products. Furthermore, the alcohol was transformed into the bromohydrin, but hydrogen bromide could not be detached from the latter with an alcoholic alkali either – the bromine was replaced by a hydroxyl group, and the initial alcohol was reconstituted.

We subjected the acetates of α-cyclopentylethanol and β-cyclopentylethanol to pyrolysis, and in both cases we synthesized the same hydrocarbon, which proved to be vinylcyclopentane:



no matter whether we started with the acetate of the primary alcohol or the acetate of the secondary alcohol. The structure of the hydrocarbon was proved by hydrogenating it, which yielded ethylcyclopentane, and by oxidizing it with permanganate (by the Wagner method), which yielded cyclopentanecarboxylic and formic acids.

Investigation of combined light-scattering spectra of the preparations synthesized from the acetate of the primary alcohol and from the acetate of the secondary alcohol uniformly indicated that the two preparations were identical, the synthesized hydrocarbon belongs to the cyclopentane series, and the double bond corresponds to a monosubstituted ethylene. Hence, this optical investigation likewise proved that the synthesized hydrocarbon has the structure of vinylcyclopentane.

Thus, the pyrolysis of the acetates was selective in the instances investigated; not only was there no ring isomerization, but the splitting off of acetic acid groups took place only in one direction; such singularity of direction is rare in the direct dehydration of alcohols.

The constants of vinylcyclopentane differ from those of the other known cyclopentane hydrocarbons with the formula $C_7H_{12}$, as is shown by the table.

## EXPERIMENTAL

α-Cyclopentylethanol was synthesized from cyclopentylmagnesium chloride and acetaldehyde [14], the yield being 33%.

| | Hydrocarbon | Boiling point | $d_4^{20}$ | $n_D^{20}$ | Source |
|---|---|---|---|---|---|
| | Ethylcyclopentene-1 | 106.5-107° | 0.8041 at 15° | 1.4429 at 21° | [14] |
| | Ethylcyclopentene-2 | 99-103° | 0.7874 | 1.4303 | [15] |
| | Ethylidenecyclopentane | 113-117° | 0.8020 | 1.4481 | [3] |
| | Vinylcyclopentane | 98.3 | 0.7796 | 1.4365 | Present paper |
| | Ethylcyclopentene-3 | Not described in the literature | | | |

B.p. 73-76° (32-30 mm); $d_4^{20}$ 0.9228; $n_D^{20}$ 1.4560; $MR_D$ 33.61.
$C_7H_{14}O$. Computed: $MR_D$ 33.85.

β-Cyclopentylethanol was synthesized from cyclopentylmagnesium chloride and ethylene oxide [17], the yield being 27%:

B.p. 94-96° (24 mm); $d_4^{20}$ 0.9190; $n_D^{20}$ 1.4576; $MR_D$ 33.85.
$C_7H_{14}O$. Computed: $MR_D$ 33.85.

The acetates were prepared by reacting the alcohols with acetic anhydride in the presence of a small quantity of orthophosphoric acid [18]. 10 parts by weight of the alcohol and 7 parts by weight of freshly distilled acetic anhydride are placed in a flask fitted with a stirrer, a reflux condenser, a dropping funnel, and a thermometer. With the stirrer in constant operation, 1 part by weight of a mixture consisting of 90 parts of acetic anhydride and 10 parts of orthophosphoric acid (sp. gr. 1.7; the mixture is prepared the day before it is to be used) is added drop by drop during the course of 20 minutes. Stirring is continued for another 2 hours after the mixture has been added. The mixture is chilled during the reaction, with the temperature prevented from rising above 38°. The reaction product is poured into water, and the oily layer is removed, washed with a soda solution and with water, and desiccated with calcium chloride, after which it is repeatedly distilled in vacuum.

The yield of the acetate of α-cyclopentylethanol was 84%. This is a colorless liquid with a pleasant, though rather sharply fruity, odor:

B.p. 76-79° (24 mm); 179-183° (746 mm); $d_4^{20}$ 0.9408; $n_D^{20}$ 1.4361; $MR_D$ 43.35
$C_9H_{16}O_2$. Computed: $MR_D$ 43.21.

The yield of the acetate of β-cyclopentylethanol was 93.5%. This is a colorless liquid with a fruity odor that is more agreeable than the odor of the acetate of the secondary alcohol:

B.p. 98-100° (34-35 mm); 193-195° (742 mm); $d_4^{20}$ 0.9541; $n_D^{20}$ 1.4399; $MR_D$ 43.18.
$C_9H_{16}O_2$. Computed: $MR_D$ 43.21.

Pyrolysis of the acetates was effected by a gentle current of nitrogen in a catalytic tube of molybdenum glass. The tube diameter was 1.4 cm, and its operative section was 45 cm long. 11.2 g of glass wool was placed in the tube. The acetates were fed through at the rate of 5-6 ml per hour. The temperature used was 500°. 59 g of the acetate of α-cyclopentylethanol was subjected to pyrolysis. The yield of the hydrocarbon was 81% after boiling over sodium. The acetate of β-cyclopentylethanol, 72.6 g of which was used, yielded 37.4 g of a hydrocarbon (after boiling over sodium), or 83.9% of the theoretical yield.

Vinylcyclopentane. Each of the pyrolysis products was distilled into a tower filled with open metallic rings, with an efficiency of approximately 40 theoretical trays. In both cases we secured products with absolutely identical properties. The properties of vinylcyclopentane are as follows:

B.p. 98.2-98.5° (750 mm); $d_4^{20}$ 0.7796; $n_D^{20}$ 1.4365; $MR_D$ 32.07.

$C_7H_{12}$. Computed: $MR_D$ 31.86.

Hydrocarbon prepared by pyrolyzing the acetate of α-cyclopentylethanol:

9.17 mg substance: 29.42 mg $CO_2$; 10.40 mg $H_2O$.
7.30 mg substance: 23.49 mg $CO_2$; 8.41 mg $H_2O$.
Found %: C 87.55, 87.38; H 12.40, 12.90.

Hydrocarbon prepared by pyrolyzing the acetate of β-cyclopentylethanol:

8.11 mg substance: 25.96 mg $CO_2$; 9.20 mg $H_2O$.
8.69 mg substance: 27.84 mg $CO_2$; 9.83 mg $H_2O$.
Found %: C 87.36, 87.58; H 12.68, 12.65.
$C_7H_{12}$. Computed %: C 87.41; H 12.59.

Hydrogenation of vinylcyclopentane was effected in the liquid phase in the cold, in the presence of platinized charcoal. 5.36 g of the hydrocarbon was used. 1321 ml (22°, 756 mm) of hydrogen was absorbed, equivalent to 1216 ml at standard conditions. 1251 ml should have been absorbed. The properties of the ethylcyclopentane synthesized were as follows:

B.p. 102.8-103.4° (756 mm); $d_4^{20}$ 0.7667; $n_D^{20}$ 1.4191; $MR_D$ 32.29.

$C_7H_{14}$. Computed: $MR_D$ 32.33.
Literature data [19]: B.p. 103.7° (760 mm); $d_4^{20}$ 0.7660; $n_D^{20}$ 1.4200.

Oxidation of vinylcyclopentane was effected in the cold with a 1% aqueous solution of permanganate and constant stirring. 4.5 g of the hydrocarbon was subjected to oxidation. No neutral oxidation products were found. Formic acid was detected in the mixture of acids by the calomel method. When the acids were distilled the temperature suddenly jumped to 215° after a few drops of the first runnings had passed over at about 100°. This yielded 1.4 g of cyclopentanecarboxylic acid with the following properties:

B.p. 215-220°; $d_4^{20}$ 1.0597; $n_D^{20}$ 1.4545.

Literature data [20]; B.p. 215.5-216°; $d_4^{20}$ 1.0510; $n_D^{18}$ 1.4534.

Analysis of the silver salt:

0.0540 g substance: 0.0261 g Ag.
0.1906 g substance: 0.0916 g Ag.
0.0231 g substance: 0.0113 g Ag.
Found %: Ag 48.33, 48.06, 48.91.
$C_6H_9O_2Ag$. Computed %: Ag 48.81.

The chemical analysis of the synthesized hydrocarbon indicates that it is vinylcyclopentane.

Results of the optical analysis of vinylcyclopentane. Both preparations (from the primary and secondary alcohols) were analyzed by the method of combined light scattering, their spectra proving to be identical. This signifies that the same hydrocarbon was synthesized in each experiment. Spectrum analysis led us to conclude, independently of the chemical analysis, that this hydrocarbon is vinylcyclopentane.

The spectrum combined light-scattering of vinylcyclopentane is: $\Delta\nu$ $cm^{-1}$ (*), 176(2d), 213(2d), 233(3d), 250(3d), 278(7d), 298(7d), 332(5d), 349(5d), 434(40), 472(1d), 489(1d), 505(1d), 559(2d·), 607(2d·), 632(3d·), 655(3d·), 707(2d·), 792(2d·), 861(27 db), 891(57), 907(15), 942(1), 968(12), 992(12), 1030(28), 1072(10), 1107(9), 1143(1··), 1168(1··), 1182(1··), 1244(1··), 1294(72), 1518(2), 1556(9 db), 1420(39), 1448(42), 1476(0), 1640(154), 2868(140), 2878(18), 2952(110), 2995(150), 3079(140).

In fact, the frequency of the double bond in the synthesized hydrocarbon, 1640 $cm^{-1}$, happens to correspond to the frequency of the double bond in monosubstituted ethylene [21]:

| | | | |
|---|---|---|---|
| 1621 | $cm^{-1}$ | for | $H_2C=CH_2$; |
| 1641 | " | " | $RHC=CH_2$; |
| 1658 | " | " | RHC=CHR-cis; |
| 1674 | " | " | RHC=CHR-trans, |

where R is not a halogen. The spectrum of the synthesized hydrocarbon also has other intensive frequencies that are characteristic of monosubstituted ethylene: 434(40), 1294(72), etc. [22]. On the other hand, the spectrum has the intensive fundamental pulsating frequency of the cyclopentane ring: 891(57), which persists, as we know, in all monosubstituted cyclopentanes.***

Inasmuch as the hydrocarbon in question is an altogether new complex molecule, it is natural that its spectrum exhibits a number of frequencies that differ from those of ethylene as well as cyclopentane hydrocarbons; but the spectrum of this molecule retains the above-mentioned frequencies of ethylene and cyclopentane that are characteristic of them.

We wish to express our profound thanks to Academician B.A.Kazansky for his continuing interest in this research and for much valuable advice.

## SUMMARY

1. Vinylcyclopentane, not previously described in the literature, has been synthesized in two ways: by pyrolysis of the acetate of α-cyclopentylethanol and pyrolysis of the acetate of β-cyclopentylethanol.

2. The frequencies of the combined light-scattering spectrum of vinylcyclopentane are listed, demonstrating its structure, in addition to the pertinent chemical reactions.

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* Against the band background.

** Center of broadly diffused lines – a band; d = diffusion line. Intensities are given in the cyclohexane scale, on which the intensity of the 802 $cm^{-1}$ line is taken as 750. The method of spectrum analysis is given in one of our previous papers [23].

*** This frequency is somewhat higher in the cyclopentene ring; moreover, in monosubstituted cyclopentenes the frequency of the double bond is considerably higher than in the hydrocarbon we have investigated.

3. This pyrolysis of the acetates enabled us to perform the reaction selectively, whereas the direct dehydration of α-cyclopentylethanol does not yield the desired results, according to the data in the literature.

4. The acetates of α-cyclopentylethanol and β-cyclopentylethanol have been synthesized and identified for the first time.

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# ABSORPTION SPECTRA AND STRUCTURES OF ANTIPYRETIC DERIVATIVES OF PHENYLHYDRAZINE

## I. β-ACYL DERIVATIVES OF PHENYLHYDRAZINE

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It is the aim of the present paper to work out the syntheses of the valuable antipyretic dihydroxypyramidon, to study its ultraviolet absorption spectra, and to compare the results obtained with its pharmacological properties.

In the second section of this paper, N.A.Valyashko and V.I.Bliznyukov [18] took part in the research, proving by their spectrographic investigation of the N-phenyl derivatives of pyrazolone that phenylhydrazine yields two saturated structures: the hydrazo and the diazo structures. The structure corresponding to the hydrazo structure of phenylhydrazine was demonstrated by the absorption spectra of both antipyrine and pyramidon, and the hypothesis was advanced that the complex ion in the molecules of these compounds that corresponds to the hydrazo structure of phenylhydrazine possesses the antipyretic properties of antipyrine and pyramidon. It was also conjectured that in this instance the toxic properties of phenylhydrazine are diminished by the closing of the pyrazolone ring. But in 1929 Scharonnat and Delaby [3], by carefully oxidizing pyramidon, synthesized dihydroxypyramidon, with an open pyrazolone ring, the antipyretic properties of pyramidon, and even less toxicity.

In order to clear up the problem of the fine structure of dihydroxypyramidon as a derivative of phenylhydrazine, we explored its absorption spectra, but since the absorption spectra of dihydroxypyramidon could not be interpreted directly, we made a systematic spectrographic analysis of the beta and alpha mono- and diacyl derivatives of phenylhydrazine. This also interested us because of the fact that some of the beta acyl derivatives of phenylhydrazine: hydracetin, cryogenin, and maretin, had also been put forward as antipyretic substances, the latter two having found fairly wide acceptance.

### Beta Acyl Derivatives of Phenylhydrazine (Syntheses)

#### β-Acetylphenylhydrazine (Hydracetin or Pyrodin)

We synthesized β-acetylphenylhydrazine by the E. Fischer [1] and O. Widman [2] method of heating phenylhydrazine with acetic anhydride, which produces a high yield.

$$C_6H_5\text{-}NH\text{-}NH_2 + (CH_3\text{-}CO)_2O \longrightarrow C_6H_5\text{-}NH\text{-}NHCOCH_3 + CH_2COOH$$

*. Extract from a candidate's dissertation by I. T. Depshko, defended at the Kharkov Pharmaceutical Institute in May, 1941.

The product was purified by fivefold crystallization from dilute alcohol. Yield: 83%. The crystals were colorless, odorless needles with a m.p. of 128.5°, readily soluble in water and alcohol.

β-β-Methylacetylphenylhydrazine

β,β-Methylacetylphenylhydrazine was prepared from dihydroxypyramidon by partial hydrolysis, according to the method due to Scharonnat and Delaby [3]:

Dihydroxypyramidon β,β-Methylacetylphenylhydrazine

The synthesized substance was purified by recrystallization from dilute alcohol.

β,β-Methylacetylphenylhydrazine consists of colorless, odorless crystals hardly soluble in water and petroleum ether, with a m.p. of 94°; Scharonnat and Delaby [3] give the m.p. as 93°, and G. Ebert and B. Reuter [4] give the m.p. as 94°. Yield: 70%.

β-Phenylsemicarbazide (Phenylhydrazide of Carbamic Acid, or Cryogenin)

E. Fischer [1] synthesized cryogenin by reacting phenylhydrazine hydrochloride with potassium cyanate. We synthesized β-phenylsemicarbazide from phenylhydrazine by heating it with urea, as given by Pinner [5], or with ethylurethane, as given by Skinner and Ruhemann [6].

$$C_6H_5-NH-NH_2\cdot HCl + H_2N-CO-NH_2 \longrightarrow C_6H_5-NH-NH-CO-NH_2 + NH_4Cl.$$

The resulting crystals were purified by repeated recrystallization from alcohol and were desiccated in a vacuum exsiccator over calcium chloride. Yield: 87%.

The S. Skinner and S. Ruhemann method [6] yields β-phenylsemicarbazide in the following reaction:

$$C_6H_5-NH-NH_2 + C_2H_5O-CO-NH_2 \longrightarrow C_6H_5-NH-NH-CO-NH_2 + C_2H_5OH.$$

Yield: 82%. The cryogenin synthesized by either method is a crystalline powder with a m.p. of 171°. The cryogenin with a m.p. of 171° is soluble in hot water, alcohol, ether, chloroform, and acetic acid [5,6].

β-(m-Tolyl)-semicarbazide (m-Tolylhydrazide of Carbamic Acid, or Maretin)

This synthesis was performed in accordance with the Mayer patent [7]: 31.6 g of m-tolylhydrazine and 24 g of urea were heated to 160° over an oil bath:

$$CH_3-C_6H_4-NH-NH_2\cdot HCl + H_2N-CO-NH_2 \longrightarrow NH_4Cl + CH_3-C_6H_4-NH-\underset{\displaystyle H_2N-CO-NH}{}$$

The product was crystallized from water and then repeatedly from alcohol. Yield: 85%.

Maretin is a white crystalline powder with a m.p. of 184° (The Bayer firm gives the m.p. as 184° [8]), which is hardly soluble in cold water, readily soluble in boiling water and alcohol, and insoluble in ether and chloroform.

## Absorption Spectra

### Research Methods [9,10]

The absorption spectra were investigated [with a quartz spectograph ($\varepsilon$ = 316)] fitted with a wavelength scale, and with an $H_{18}$ logarithmic sectorphotometer made by the firm of Hilger [10].

Investigation of absorption at the short wavelength of $\lambda$ = 2250Å was done by means of a film smeared, before exposure, with good vaseline oil, which was washed off with petroleum ether just before exposure.

According to Rossler [11], Stucklen [12], and Weigert [13], mineral oil sensitizes ordinary films.

### Purifying the Solvents

Ethyl alcohol was purified by distilling it twice into a Hempel tower 100 cm high, the middle fraction always being taken. The alcohol thus prepared was placed in a 1-cm tube, and light passed through down to about $\lambda$ = 2250 Å

Hexane was prepared from petroleum ether by the Menzel method [14].

A layer of the purified hexane 1 cm thick passes light down to about $\lambda$ = 2060 Å. The water for these tests was prepared by double distillation.

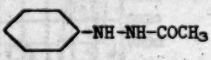
This is the first time that dichlorethane has been employed in spectrographic analysis.

The dichloroethane prepared for spectrographic use was purified by agitating it with sulfuric acid containing 8-10% of sulfuric anhydride. The dichloroethane is then a colorless liquid with an odor like that of chloroform.

A layer 1 cm thick passes light down to about $\lambda$ = 2200 Å.

### Spectrographic Analysis

#### β-Acetylphenylhydrazine (Hydracetin, Pyrodin)




D. Biquard [15] was the first to make a quantitative spectrographic analysis of β-acetylphenylhydrazine in alcoholic solution, doing so while engaged in a study of phenylhydrazine and its derivatives. She discovered two well-marked bands with maxima at approximately $\lambda$ = 2810 Å and $\lambda$ = 2330 Å.

We subjected β-acetylphenylhydrazine to more detailed investigation in alcohol, hexane, alcoholic solutions of hydrogen chloride, and sodium alcoholate.

#### β-Acetylphenylhydrazine in Hexane, $5 \cdot 10^{-4}$ to $5 \cdot 10^{-5}$ Mol

(Fig. 1, Curve 2).

The curve begins at $\lambda$ = 3000 Å and $\varepsilon$ = 200, being shifted 30Å toward the visible region from the alcohol curve (Fig 1, Curve 1), and exhibits a band maximum $g_1$ at $\lambda$ = 2825 Å and $\varepsilon$ = 1000, shifted 45 Å toward the ultraviolet and 2.3 times lower than the alcohol curve. Then the curve turns upward, exhibiting a band maximum $g_2$ at $\lambda$ = 2315 Å and $\varepsilon$ = 8000, shifted 20 Å toward the ultraviolet as compared to the alcohol curve, and ends at $\lambda$ = 2190 Å and $\varepsilon$ = 2000. The $g_1$ and $g_2$ bands are somewhat displaced in opposite directions and somewhat drawn apart, forming a deeper minimum.

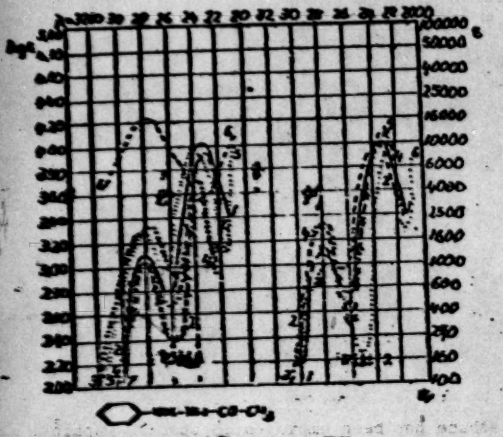


Fig. 1 - β-acetylphenylhydrazine in alcohol, from $10^{-3}$ to $10^{-4}$ mol; 2 - the same in benzene, from $5 \cdot 10^{-4}$ to $5 \cdot 10^{-6}$ mol; 3 - the same in alcohol, from $10^{-3}$ to $10^{-4}$ mol, + 10-molal $NaOC_2H_5$; 4 - the same in 2-molal $NaOC_2H_5$, from $10^{-3}$ to $5 \cdot 10^{-5}$ mol; 5 - phenylhydrazine in alcohol, from $10^{-2}$ to $10^{-4}$ mol; 6 - the same at $5 \cdot 10^{-5}$ mol, after 15 hours.

Fig. 2 - o-Acetylphenylhydrazine in alcohol, from $10^{-3}$ to $10^{-4}$ mol; 2 - the same, from $2 \cdot 10^{-4}$ to $2.5 \cdot 10^{-5}$ mol, after standing for 15 hours; 3- the same, from $10^{-3}$ to $10^{-4}$ + 100-molal HCl; 4- the same in 5-molal HCl, from $5 \cdot 10^{-3}$ to $5 \cdot 10^{-5}$ mol; 5- the same, from $2 \cdot 10^{-4}$ to $2.5 \cdot 10^{-5}$ mol, + 100-molal HCl, after standing for 15 hours; 6- phenylhydrazine, from $5 \cdot 10^{-4}$ mol, to $5 \cdot 10^{-5}$ mol, + 100-molal HCl.

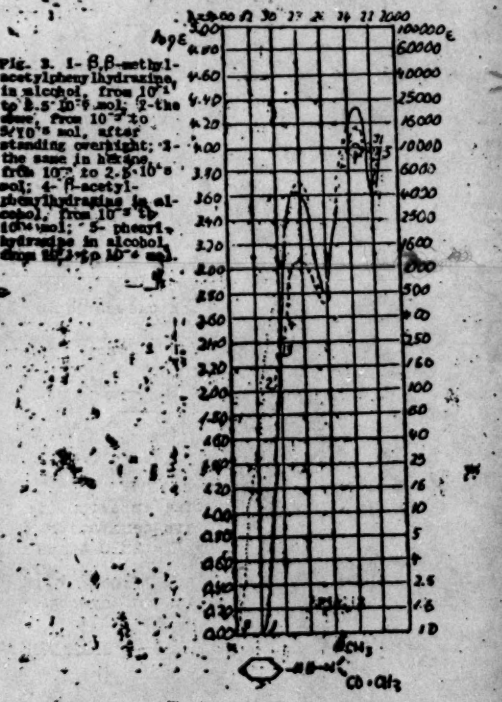


Fig. 3. 1- β,β-methylacetylphenylhydrazine in alcohol, from $10^{-3}$ to $2.5 \cdot 10^{-5}$ mol; 2-the same, from $10^{-3}$ to $5 \cdot 10^{-5}$ mol, after standing overnight; 3- the same in benzene, from $10^{-3}$ to $2.5 \cdot 10^{-5}$ mol; 4- β-acetylphenylhydrazine in alcohol, from $10^{-3}$ to $10^{-4}$ mol; 5- phenylhydrazine in alcohol, from $10^{-2}$ to $10^{-4}$ mol.

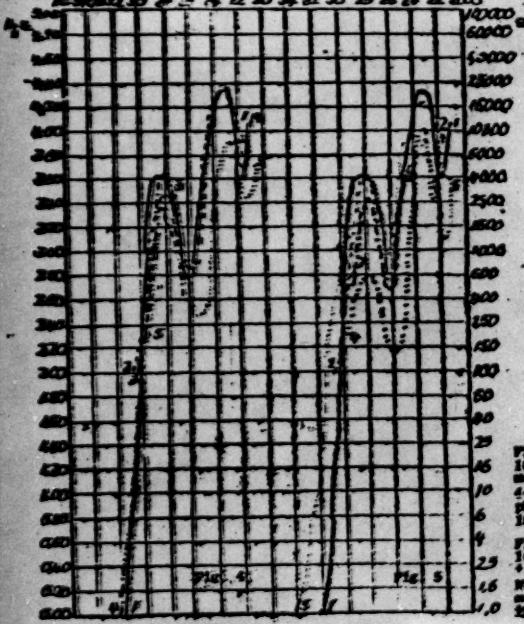


Fig. 4: 1- β,β-methylacetylphenylhydrazine in alcohol, from $10^{-3}$ to $2.5 \cdot 10^{-5}$ mol; 2- the same, from $10^{-3}$ to $2.5 \cdot 10^{-5}$ mol, + 100-molal HCl; 3- the same, after standing overnight; 4- the same in 5-molal HCl, from $10^{-3}$ to $5 \cdot 10^{-5}$ mol; 5- phenylhydrazine in alcohol, from $5 \cdot 10^{-4}$ to $5 \cdot 10^{-5}$ mol, + 100-molal HCl.

Fig. 5. 1- β,β-methylacetylphenylhydrazine in alcohol, from $10^{-3}$ to $2.5 \cdot 10^{-5}$ mol; 2- the same, from $10^{-3}$ to $5 \cdot 10^{-5}$ mol, + 10-molal $NaOC_2H_5$; 3 - the same, in 2-molal $NaOC_2H_5$, after standing for 15 hours; 4- the same, in 2-molal $NaOC_2H_5$, from $5 \cdot 10^{-4}$ to $5 \cdot 10^{-5}$ mol; 5- phenylhydrazine in alcohol, from $10^{-2}$ to $10^{-4}$ mol.

TABLE 1

β-Acetylphenylhydrazine in Hexane, $5 \cdot 10^{-4}$ to $5 \cdot 10^{-5}$ Mol (Fig. 1, Curve 2)

| λ | ε | λ | ε | λ | ε |
|---|---|---|---|---|---|
| 3000 | 200 | 2680 | 320 | 2370 | 7000 |
| 2940 | 600 | 2650 | 260 | 2350 | 8000 |
| | | min. | | max. | |
| 2900 | 800 | 2550 | 260 | 2280 | 8000 |
| 2880 | 1000 | 2530 | 320 | 2270 | 7000 |
| max. | | | | | |
| 2770 | 1000 | 2480 | 1000 | 2190 | 2000 |
| 2750 | 800 | 2440 | 3200 | | |

TABLE 2

β-Acetylphenylhydrazine in Alcohol, $10^{-3}$ to $10^{-4}$ Mol (Fig. 1, Curve 1)

| λ | ε | λ | ε | λ | ε |
|---|---|---|---|---|---|
| 3000 | 100 | 2670 | 600 | 2455 | 5000 |
| | | min. | | | |
| 2905 | 800 | 2620 | 600 | 2410 | 8000 |
| 2890 | 1000 | 2590 | 700 | 2365 | 10000 |
| max. | | | | max. | |
| 2730 | 1000 | 2580 | 800 | 2300 | 10000 |
| 2715 | 800 | 2570 | 1000 | 2250 | 8000 |
| 2690 | 700 | 2500 | 3000 | 2140 | 2500 |

β-Acetylphenylhydrazine in Alcohol, $10^{-3}$ to $10^{-4}$ Mol (Fig. 1, Curve 1)

This gives a curve that starts at $\lambda$ = 3200 A and $\varepsilon$ = 100, shifted 160 A toward the short-wave end of the spectrum compared to the curve of phenylhydrazine in alcohol (Fig. 1, Curve 5) and running parallel to the latter, with a band maximum $g_1$ at $\lambda$ = 2810 A and $\varepsilon$ = 1000, approximately 1.5 times less intense. The curve then drops to a minimum at $\lambda$ = 2645 A and $\varepsilon$ = 600 and, rising again, exhibits a second band maximum $g_2$ at $\lambda$ = 2333 A and $\varepsilon$ = 10,000, which is likewise shifted 82 A toward the ultraviolet, and ends at $\lambda$ = 2140 A and $\varepsilon$ = 2500. According to our data, the absorption spectrum of β-acetylphenylhydrazine in alcohol coincides within the limits of experimental error with that found by D. Biquard [15].

β-Acetylphenylhydrazine in Alcohol, $2 \cdot 10^{-4}$ to $2 \cdot 10^{-5}$ Mol. (Fig. 2, Curve 2)

Inasmuch as N.A.Valyashko and V.I.Blizhyukov [16] had found, in their investigation of phenylhydrazine in alcohol, that its spectrum changed when its solutions were allowed to stand, we also made an investigation of β-acetylphenylhydrazine after it had stood for 15 hours. Compared to the alcohol curve plotted immediately after dissolution (Fig. 1, Curve 1), the curve is shifted 45 A toward the longer wavelengths, likewise constituting two bands: $g_1$ at $\lambda$ = 2800 A and $\varepsilon$ = 900 and $g_2$ at $\lambda$ = 2355 A and $\varepsilon$ = 10,000; the $g_1$ band is twice as intensive and is close to the band for phenylhydrazine in alcohol investigated immediately after dissolution.

β-Acetylphenylhydrazine in alcohol, from $10^{-3}$ to $10^{-4}$ mol, + 100 mols of HCl (Fig. 2, Curve 3) is shifted 90 A with respect to the alcohol curve (Fig. 2, Curve 1) and constitutes a band maximum $g_1$ at $\lambda$ = 2800 A and $\varepsilon$ = 1000 and another $g_2$ at $\lambda$ = 2315 A and $\varepsilon$ = 10,000.

The curve of β-acetylphenylhydrazine in alcohol + 100 mols of HCl is like the curve in alcohol, but its displacement toward the ultraviolet with respect to the curve for phenylhydrazine in alcohol (Fig. 1, Curve 5) is smaller. The band maximum $g_1$ is twice as high on the curve of β-acetylphenylhydrazine in alcohol + 100 mols of HCl after 15 hours of standing (Fig. 2, Curve 4).

β-Acetylphenylhydrazine in 5 mols of HCl, from $5 \cdot 10^{-4}$ to $5 \cdot 10^{-5}$ (Fig. 2, Curve 5).

The curve is shifted 30 A toward the ultraviolet compared to that recorded with 100-molal HCl immediately after it had been added (Fig. 2, Curve 3); it likewise constitutes two bands: $g_1$ at $\lambda$ = 2805 A and $\varepsilon$ = 1200, with a maximum 1.6 times lower, and $g_2$ at $\lambda$ = 2315 A and $\varepsilon$ = 12,000, which does not differ from the curve

recorded with 100 mols of HCl present within the limits of experimental error. HCl does not cause any appreciable change in the spectrum of β-acetylphenylhydrazine.

β-Acetylphenylhydrazine in alcohol, from $10^{-3}$ to $10^{-4}$ mol + 10molal $NaOC_2H_5$

(Fig. 1, Curve 3)

At ε = 100, the curve is shifted 220 Å toward the visible region with respect to the alcohol curve; it exhibits a band maximum $\varepsilon_1$ at λ = 2765 Å and ε = 2000 that is twice as intense as in the alcohol curve (Fig. 1, Curve 3) and a band maximum $\varepsilon_2$ at λ = 2375 Å and ε = 4000, that is shifted only 42 Å but is 2.5 times less intense; it ends at λ = 2250 and ε = 1000.

TABLE 3

β-Acetylphenylhydrazine in Alcohol, From $10^{-3}$ to $10^{-4}$ Mol + 100 Molal HCl (Fig. 2, Curve 3)

| λ | ε | λ | ε | λ | ε |
|---|---|---|---|---|---|
| 3090 | 100 | 2660 | 700 | 2350 max. | 10000 |
| 2930 | 800 | 2650 min. | 600 | 2280 | 10000 |
| 2870 max. | 1000 | 2590 | 600 | 2250 | 8000 |
| 2730 | 1000 | 2575 | 700 | 2180 | 3000 |
| 2680 | 800 | 2415 | 8000 | | |

β-Acetylphenylhydrazine in 2 Molal Sodium Alcoholate, From $10^{-3}$ Mol to $5 \cdot 10^{-5}$ Mol (Fig. 1, Curve 4)

Compared to the curve for alcohol, this curve is displaced 60 Å toward the longer wavelengths; it rises, intersects the alcohol curve, and moves toward the ultraviolet, forming a $\varepsilon_1$ band with a maximum λ = 2805 Å and ε = 800 and a $\varepsilon_2$ band at λ = 2310 Å and ε = 3500. Compared to the alcohol curve, the $\varepsilon_2$ band is 2.8 times lower.

TABLE 4

β-Acetylphenylhydrazine in Alcohol, From $2 \cdot 10^{-4}$ to $2.5 \cdot 10^{-5}$ Mol, + 100-Molal HCl, After Standing 15 Hours (Fig. 2, Curve 4).

| λ | ε | λ | ε | λ | ε |
|---|---|---|---|---|---|
| 2980 | 500 | 2720 | 1000 | 2550 | 1000 |
| 2900 | 1500 | 2700 | 650 | 2450 | 8000 |
| 2850 max. | 1750 | 2690 min. | 500 | 2360 max. | 10000 |
| 2750 | 1750 | 2580 | 500 | 2270 | 10000 |
| 2740 | 1500 | 2570 | 650 | 2150 | 2800 |

TABLE 5

β-Acetylphenylhydrazine in Molal HCl, from $5 \cdot 10^{-4}$ to $5 \cdot 10^{-5}$ Mol. (Fig. 2, Curve 5)

| λ | ε | λ | ε | λ | ε |
|---|---|---|---|---|---|
| 3000 | 200 | 2650 min. | 320 | 2290 max. | 18000 |
| 2850 max. | 1200 | 2590 | 320 | 2240 | 5000 |
| 2760 | 1200 | 2340 max | 12000 | 2220 | 2600 |

β-Acetylphenylhydrazine in alcohol yielded a curve (Fig. 1, Curve 3) under the action of 10 molal sodium alcoholate, on which the $\varepsilon_1$ band is wider and twice as intensive, while the $\varepsilon_2$ band, on the other hand, is narrower and less intensive; in the 2-molal solution of sodium alcoholate, the $\varepsilon_1$ band again loses intensity, and the $\varepsilon_2$ band is likewise about 3 4 times less intense than in the curve with alcohol (Fig. 1, Curve 1).

Hence, introducing an acetyl group at the beta position in phenylhydrazine makes the hydrazo structure of the latter extremely stable. The variability of the spectrum of β-acetylphenylhydrazine gives some hints of the presence of a diazo band in the spectrum, inasmuch as allowing its solutions in neutral alcohol and in the presence of HCl to stand makes the $\varepsilon_1$ band more intense and makes it approach the band of phenylhydrazine, while also making it narrower. The alcoholate makes the spectrum of β-acetylphenylhydrazine differ even more from that of phenylhydrazine,

TABLE 6

β-Acetylphenylhydrazine in Alcohol, from $10^{-3}$ to $10^{-4}$ Mol, + 10 Molal $NaOC_2H_5$ (Fig. 1, Curve 3)

| λ | ε | λ | ε | λ | ε |
|---|---|---|---|---|---|
| 3220 | 100 | 2525 min. | 1000 | 2410 max. | 4000 |
| 3000 | 1000 | 2520 | 1000 | 2360 | 4000 |
| 2835 max. | 2000 | 2480 | 1600 | 2250 | 1000 |
| 2735 | 2000 | | | | |

TABLE 7

β-Acetylphenylhydrazine in 2-Molal $NaOC_2H_5$, From $10^{-3}$ to $5 \cdot 10^{-5}$ Mol. (Fig. 1, Curve 4)

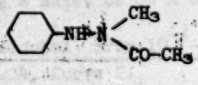
| λ | ε | λ | ε | λ | ε |
|---|---|---|---|---|---|
| 3060 | 100 | 2670 min. | 500 | 2385 max. | 3000 |
| 2860 max. | 1000 | 2570 | 500 | 2335 | 3000 |
| 2750 | 1000 | 2500 | 1000 | 2255 | 1000 |

TABLE 8

| Items | $\varepsilon_1$ | | $\varepsilon_2$ | |
|---|---|---|---|---|
| | λ | ε | λ | ε |
| β-Acetylphenylhydrazine in alcohol | 2810 | 1000 | 2333 | 10000 |
| " in hexane | 2825 | 1000 | 2315 | 8000 |
| " in alcohol, after standing for 15 hours | 2800 | 2000 | 2255 | 10000 |
| β-Acetylphenylhydrazine in alcohol + 100-molal HCl. | 2800 | 1000 | 2315 | 10000 |
| " after standing for 15 hours | 2800 | 1750 | 2315 | 10000 |
| β-Acetylphenylhydrazine in 5-molal HCl | 2805 | 1200 | 2315 | 12000 |
| in alcohol + 10-molal $NaOC_2H_5$ | 2765 | 2000 | 2375 | 4000 |
| β-Acetylphenylhydrazine in 2-molal $NaOC_2H_5$ | 2805 | 800 | 2310 | 3500 |
| " + 10-molal $NaOC_2H_5$ after standing overnight | 2800 | 2000 | 2355 | 10000 |
| Phenylhydrazine in alcohol | 2828 | 1600 | 2410 | 9000 |

possibly because of the reaction of the acetyl carbonyl group and the phenylhydrazine hydrogen atoms with the alcoholate. The diminution of the intensity of both bands in 2-molal sodium alcoholate may be due to partial hydrolysis of the β-acetylphenylhydrazine.

β-β-Methylacetylphenylhydrazine




We are the first to have investigated the absorption spectra of β,β-methylacetylphenylhydrazine; we did so in hexane, alcohol, alcoholic solutions of hydrogen chloride, and sodium alcoholate of various concentrations and under various conditions.

β,β-Methylacetylphenylhydrazine in Hexane, From $10^{-3}$ to $2.5 \cdot 10^{-5}$ Mol (Fig. 3, Curve 3)

In view of the slight solubility of β,β-methylacetylphenylhydrazine in hexane,

we began our investigation at $\varepsilon = 100$. The curve begins at $\lambda = 2995$ Å and $\varepsilon = 100$, rising and exhibiting a $\varepsilon_1$ band with a maximum at $\lambda = 2830$ Å and $\varepsilon = 4000$ and a $\varepsilon_2$ band with a maximum at $\lambda = 2320$ Å and $\varepsilon = 16{,}000$, and a minimum at $\lambda = 2218$ Å and $\varepsilon = 5200$ (Table 9).

When we compare the curves of β,β-methylacetylphenylhydrazine in alcohol and in hexane (Fig. 3, Curves 1 and 3), we find no essential differences. The $\varepsilon_1$ band maxima coincide, and the minimum following the $\varepsilon_2$ band is lowered somewhat. The $\varepsilon_2$ band maximum is 1.25 times greater, with the minimum lowered and displaced 10 Å toward the ultraviolet in the hexane.

β,β-Methylacetylphenylhydrazine in Alcohol, From $10^{-1}$ to $2.5 \cdot 10^{-5}$ Mol (Fig. 3, Curve 1)

The curve starts at $\lambda = 3190$ Å and $\varepsilon = 1$, and rises, forming a $\varepsilon_1$ band maximum at $\lambda = 2830$ Å and $\varepsilon = 4000$ and a $\varepsilon_2$ band maximum at $\lambda = 2230$ Å and $\varepsilon = 20{,}000$; after passing through a minimum at $\lambda = 2190$ Å and $\varepsilon = 4000$, it rises, ending at $\lambda = 2130$ and $\varepsilon = 10{,}000$ (Table 10).

TABLE 9

β'β-Methylacetylphenylhydrazine in Hexane, From $10^{-3}$ to $2.5 \cdot 10^{-5}$ Mol. (Fig 3, Curve 3)

| λ | ε | λ | ε | λ | ε |
|---|---|---|---|---|---|
| 2995 | 100 | 2635 min. | 700 | 2340 max. | 16000 |
| 2945 | 1000 | 2580 | 700 | 2300 | 16000 |
| 2860 max. | 4000 | 2380 | 10000 | 2235 min. | 5200 |
| 2810 | 4000 | 2360 | 14000 | 2190 | 5200 |

TABLE 10

β,β-Methylacetylphenylhydrazine in Alcohol, from $10^{-1}$ to $2.5 \cdot 10^{-5}$ Mol. (Fig. 3, Curve 1)

| λ | ε | λ | ε | λ | ε |
|---|---|---|---|---|---|
| 3190 | 1 | 2860 max. | 4000 | 2370 max. | 20000 |
| 3080 | 10 | 2800 | 4000 | 2290 | 20000 |
| 3010 | 100 | 2630 min. | 600 | 2210 min. | 4000 |
| 2930 | 1000 | 2600 | 600 | 2170 | 4000 |
| 2920 | 3000 | 2570 | 1000 | 2130 | 10000 |

The curve of β,β-methylacetylphenylhydrazine in alcohol, from $10^{-3}$ to $5 \cdot 10^{-5}$ mol, after standing overnight, (Fig. 3, Curve 2), exhibited no changes in the absorption spectrum. Introducing a methyl group at the beta position in β-acetylphenylhydrazine (Fig. 3, Curves 1 and 4) increases the $\varepsilon_1$ band maximum of β-acetylphenylhydrazine by a factor of 4 and the $\varepsilon_2$ band maximum by a factor of 2.

When we compare β,β-methylacetylphenylhydrazine in alcohol with phenylhydrazine in alcohol (Fig. 3, Curves 1 and 5), we see that substituting a methyl and an acetyl group for the hydrogen atoms increases the $\varepsilon_1$ band by a factor of 2.5 and the $\varepsilon_2$ band by a factor of 2, as well as effecting a shift of 80 Å toward the longer wavelengths.

β,β-Methylacetylphenylhydrazine in Alcohol, From $10^{-3}$ to $2.5 \cdot 10^{-5}$ Mol, + 100 Molal HCl (Fig. 4, Curve 2).

The curve starts at $\lambda = 3030$ Å and $\varepsilon = 100$ and rises, passing through a $\varepsilon_1$ band maximum at $\lambda = 2830$ Å and $\varepsilon = 2000$, this band being somewhat narrower than that on the curve for neutral alcohol (Fig. 4, Curve 1) and half as intense; the $\varepsilon_2$ band exhibits a maximum at $\lambda = 2328$ Å and $\varepsilon = 24{,}000$ and almost coincides with that on the curve for alcohol without any acid (Table 11).

β,β-Methylacetylphenylhydrazine in Alcohol, From $10^{-3}$ to $2.5 \cdot 10^{-5}$ Mol, + 100 Molal HCl, After Standing Overnight (Fig. 4, Curve 3).

The maximum of the $g_1$ band is twice as high and is shifted 30 A toward the ultraviolet, as compared with Curve 1, which was plotted immediately, without letting the solution stand; the minimum of this band is 1.5 times lower and shifted 25 A toward the longer wavelengths.

Comparing the curve for β,β-methylacetylphenylhydrazine in 100-molal HCl with the curve for phenylhydrazine (Fig. 4, Curves 2 and 6), we found that when the methyl and the acetyl group are introduced into phenylhydrazine at the beta position, the $g_1$ band on the curve is twice as big and is shifted 65 A toward the longer wavelengths, while the maximum of the $g_2$ band is 3.1 times as big and is shifted 58 A toward the longer wavelengths (Table 12).

TABLE 11

β,β-Methylacetylphenylhydrazine, From $10^{-3}$ to $2.5 \cdot 10^{-5}$ Mol, + 100-Molal HCl (Fig. 4, Curve 2)

| λ | | λ | ε | λ | ε |
|---|---|---|---|---|---|
| | | | | max. | |
| 3050 | 100 | 2630 | 600 | 2285 | 24000 |
| 2935 | 1000 | 2590 | 600 | 2200 | 10000 |
| | | min. | | | |
| 2870 | 2000 | 2555 | 1000 | 2170 | 6400 |
| max. | | | | min. | |
| 2790 | 2000 | 2425 | 16000 | 2150 | 6400 |
| 2690 | 1000 | 2370 | 24000 | 2130 | 10000 |
| | | max. | | | |

TABLE 12

β,β-Methylacetylphenylhydrazine, in Alcohol, from $10^{-5}$ to $2.5 \cdot 10^{-5}$ Mol., + 100-Molal HCl, After Standing Over Night. (Fig. 4, Curve 3)

| λ | ε | λ | ε | λ | ε |
|---|---|---|---|---|---|
| 3050 | 100 | 2700 | 1000 | 2540 | 1000 |
| 2840 | 4000 | 2600 | 4000 | 2520 | 2000 |
| max. | | min. | | | |
| 2760 | 4000 | 2610 | 400 | 2470 | 5000 |

TABLE 13

β,β-Methylacetylphenylhydrazine in 5-Molal HCl, From $10^{-1}$ to $5 \cdot 10^{-5}$ Mol. (Fig. 4, Curve 4)

| λ | ε | λ | ε | λ | ε |
|---|---|---|---|---|---|
| 3220 | 1 | 2750 | 2500 | 2390 | 20000 |
| | | | | max. | |
| 3090 | 10 | 2620 | 700 | 2280 | 20000 |
| | | min. | | | |
| 3020 | 100 | 2580 | 700 | 2180 | 4000 |
| | | | | min. | |
| 2900 | 1000 | 2520 | 2000 | 2150 | 4000 |
| 2840 | 2500 | 2425 | 10000 | 2090 | 1200 |
| max. | | | | | |

β,β-Methylacetylphenylhydrazine in 5-Molal HCl, From $10^{-1}$ to $5 \cdot 10^{-5}$ Mol. (Fig. 4, Curve 4)

The curve begins close to that for alcohol, and up to ε = 600 it is shifted toward the ultraviolet like the curve for alcohol + 100-molal HCl, forming two phenylhydrazine bands: $g_1$ and $g_2$. The maximum of the $g_1$ band is shifted 35 A toward the ultraviolet and is somewhat stronger than that for the curve plotted in the presence of 100-molal HCl, but it is 1.6 times less intense than that for the alcohol curve. The $g_2$ band practically coincides with the alcohol one throughout its expanse (Table 13).

β,β-Methylacetylphenylhydrazine in Alcohol, From $10^{-3}$ to $5 \cdot 10^{-5}$ Mol, + 10-Molal $NaOC_2H_5$ (Fig. 5, Curve 2)

No changes were observed in the curve plotted for the sodium alcoholate solution compared to the curve for alcohol, inasmuch as only the upper part of the $g_1$ band

was found to be narrower, with its maximum shifted toward the ultraviolet, in the $2 \cdot 10^{-4}$ mol solution in 10-molal $NaOC_2H_5$ (Fig. 5, Curve 2) after standing for 15 hours; the maximum of the $g_1$ band was lowered by a factor of 2.5 after standing (Tables 14 and 15).

TABLE 14

β,β-Methylacetylphenylhydrazine, From $10^{-3}$ to $5 \cdot 10^{-5}$ Mol, + 10-Molal $NaOC_2H_5$ (Fig. 5, Curve 2).

| λ | ε | λ | ε | λ | ε |
|---|---|---|---|---|---|
| 3070 | 100 | 2695 | 1000 | 2460 | 10000 |
| 2920 | 1000 | 2650 min. | 600 | 2380 max | 16000 |
| 2820 max | 4000 | 2600 | 600 | 2290 | 16000 |
| 2780 | 4000 | 2485 | 6000 | 2210 | 10000 |

TABLE 15

β,β-Methylacetylphenylhydrazine, $2 \cdot 10^{-4}$ Mol, + 10-Molal $NaOC_2H_5$ After Standing for 15 Hours. (Fig. 5, Curve 3)

| λ | ε | λ | ε | λ | ε |
|---|---|---|---|---|---|
| | | max. | | | |
| 2910 | 500 | 2765 | 2500 | 2580 | 1000 |
| 2880 | 1000 | 2670 min. | 500 | 2530 | 2000 |
| 2815 max. | 2500 | 2610 | 500 | 2470 | 4000 |

Methylacetylphenylhydrazine in a 2-Molal Solution of Sodium Alcoholate, From $5 \cdot 10^{-4}$ to $5 \cdot 10^{-3}$ Mol. (Fig. 5, Curve 4)

In the bimolal alkali, the absorption curve of β,β-methylacetylphenylhydrazine drops, producing a $g_1$ band with a maximum at λ = 2805 Å and ε = 600, which is 6.6 times as low, and a $g_2$ band with a maximum at λ = 2338 Å and ε = 10,000, which is twice as low, as the absorption recorded for alcohol.

Compared to the absorption of phenylhydrazine in alcohol, the maximum of the $g_1$ band is 2.5 times as low, and the intensity of the $g_2$ band coincides with that of the phenylhydrazine band, but is shifted 72 Å toward the ultraviolet. The displacement from the phenylhydrazine curve indicates that the hydrolysis of the β,β-methylacetylphenylhydrazine may be incomplete, thus exhibiting the effect of the alkali upon the molecule (Table 17).

Introducing the methyl group into the β-acetylphenylhydrazine, thus forming β,β-methylacetylphenylhydrazine, increases the intensity of the absorption bands of β-acetylphenylhydrazine by a factor of 4-5 for the $g_1$ band and 1.6-2 for the $g_2$ band. The nature of the hydrazo absorption of phenylhydrazine is shown even more markedly. The absorption spectrum of β,β-methylacetylphenylhydrazine is almost unaffected by hexane, alcohol, or alcoholic hydrochloric acid. β,β-Methylacetylphenylhydrazine exhibits a pronounced change in the intensity of the absorption band in a 2-molal solution of sodium alcoholate, without affecting the nature of the spectrum.

TABLE 16

β,β-Methylacetylphenylhydrazine in 2-Molal $NaOC_2H_5$, From $5 \cdot 10^{-4}$ to $5 \cdot 10^{-3}$ Mol. (Fig. 5, Curve 4)

| λ | ε | λ | ε | λ | ε |
|---|---|---|---|---|---|
| 2970 | 200 | 2580 min. | 200 | 2350 max. | 10000 |
| 2840 max. | 600 | 2520 | 200 | 2315 | 10000 |
| 2770 | 600 | 2465 | 1000 | 2260 min. | 8500 |
| 2710 | 320 | 2405 | 3200 | 2230 | 8500 |

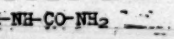
Inasmuch as the $g_1$ and $g_2$ absorption bands are related to the interaction of alpha nitrogen with the benzene ring, a change of this sort indicates that the action

of the sodium alcoholate may also affect the alpha nitrogen, diminishing its effect upon the ring, this action increasing in effectiveness with an increase in the alkali concentration, plus a possible addition of the acetyl group to the carbonyl group, with partial saponification of the former.

TABLE 17

| Items | 1 | | 2 | |
|---|---|---|---|---|
| | λ | ε | λ | ε |
| β,β-Methylacetylphenylhydrazine in hexane | 2830 | 4000 | 2320 | 16000 |
| " in alcohol | 2830 | 4000 | 2280 | 20000 |
| " in alcohol, after standing overnight | 2795 | 5000 | 2330 | 20000 |
| β,β-Methylacetylphenylhydrazine in 100-molal HCl | 2830 | 2000 | 2328 | 24000 |
| " in 5-molal HCl | 2795 | 2500 | 2335 | 20000 |
| " + 10-molal $NaOC_2H_5$ | 2800 | 4000 | 2335 | 16000 |
| " in 2-molal $NaOC_2H_5$ | 2805 | 500 | 2338 | 10000 |
| β-Acetylphenylhydrazine in alcohol | 2810 | 1000 | 2333 | 10000 |
| Phenylhydrazine in alcohol | 2828 | 1600 | 2410 | 9000 |
| + 100 molal HCl | 2765 | 1000 | 2270 | 8000 |

β-Phenylsemicarbazide (β-Phenylhydrazide of Carbamic Acid, or Cryogenin)



We are the first to have studied the spectra of β-phenylsemicarbazide. The research was carried out in alcohol, hexane, alcoholic solutions of hydrogen chloride, and sodium alcoholate. The β-phenylsemicarbazide used in the research was freshly recrystallized from alcohol, because it turned pink during storage.

β-Phenylsemicarbazide in Alcohol, From $10^{-4}$ to $5 \cdot 10^{-5}$ Mol (Fig. 6, Curve 1)

The curve starts at λ = 3260 Å and ε = 1, being shifted 110 Å toward the ultraviolet from Curve 5 in Fig. 6 (for phenylhydrazine in alcohol); it then rises, exhibiting a maximum of the $g_1$ band at λ = 2735 and ε = 1000, shifted 55 Å toward ultraviolet and by a factor of 1.6 lower than the phenylhydrazine maximum (Fig. 6, Curve 5). Then, rising, it exhibits a maximum of the $g_2$ band at λ = 2340 Å and ε = 14,000, which is also shifted 70 Å toward the ultraviolet but is 1.5 times as intense, and ends at λ = 2130 Å and ε = 6000 (Table 18).

When we compare the curve of β-phenylsemicarbazide in alcohol with that of β-acetylphenylhydrazine in alcohol (Fig. 6, Curves 1 and 4), we find (as has been pointed out above for phenylhydrazine) that the maximum of the $g_1$ band is shifted farther toward the ultraviolet, while the $g_2$ bands coincide within the limits of experimental error, though the intensity of the band is 1.4 times as great. Curve 3 (Fig. 6) shows the absorption spectrum of cryogenin in alcohol after standing overnight; the curve is close to that of phenylhydrazine, rising and exhibiting a maximum of the $g_1$ band at λ = 2785 Å and ε = 3000. The intensity of the $g_2$ band is three times as great after standing overnight and is shifted 50 Å toward the visible region, compared to the curve plotted for solution in alcohol immediately after dissolution.

The $g_2$ band coincides with that on the curve of phenylhydrazine throughout its width, deviating only below the maximum, being shifted toward the ultraviolet and ending at λ = 2150 Å and ε = 6000. The curve for β-phenylsemicarbazide in alcohol

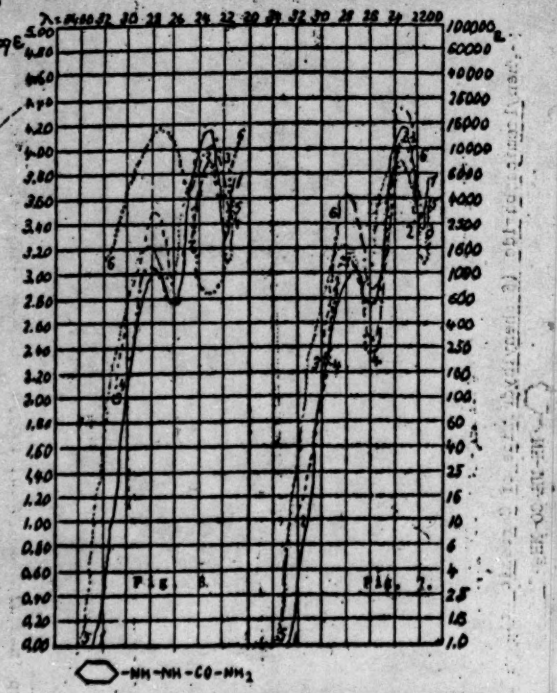



Fig. 6. 1- β-Phenylsemicarbazide in alcohol, from $10^{-1}$ to $5\cdot10^{-5}$ mol; 2-(xxx) β-phenylsemicarbazide in hexane, $5\cdot10^{-5}$ mol; 3-(---) β-phenylsemicarbazide in alcohol, from $10^{-5}$ to $5\cdot10^{-5}$ mol, after standing overnight; 4-(-·-) β-acetylphenylhydrazine in alcohol, from $10^{-5}$ to $10^{-4}$ mol; 5-(· · ·) phenylhydrazine in alcohol, from $10^{-1}$ to $10^{-4}$ mol; 6-(···) phenylhydrazine in alcohol, $5\cdot10^{-5}$ mol, after standing 18 hours.

Fig. 7. 1-β-Phenylsemicarbazide in alcohol, $10^{-4}$ to $5\cdot10^{-5}$ mol; 2-β-phenylsemicarbazide in alcohol, $10^{-2}$ to $5\cdot10^{-5}$ mol + 100-molal HCl; 3-(-·-) β-phenylsemicarbazide in 5-molal HCl, $5\cdot10^{-5}$ to $5\cdot10^{-4}$ mol; 4-(xxx) β-phenylsemicarbazide in alcohol, $5\cdot10^{-5}$ to $5\cdot10^{-4}$ mol + 2-molal HCl; 5-(· · ·) phenylhydrazine in alcohol, $10^{-1}$ to $5\cdot10^{-5}$ mol; 6-(-··-) phenylhydrazine in alcohol, $5\cdot10^{-5}$ mol + 100-molal HCl.

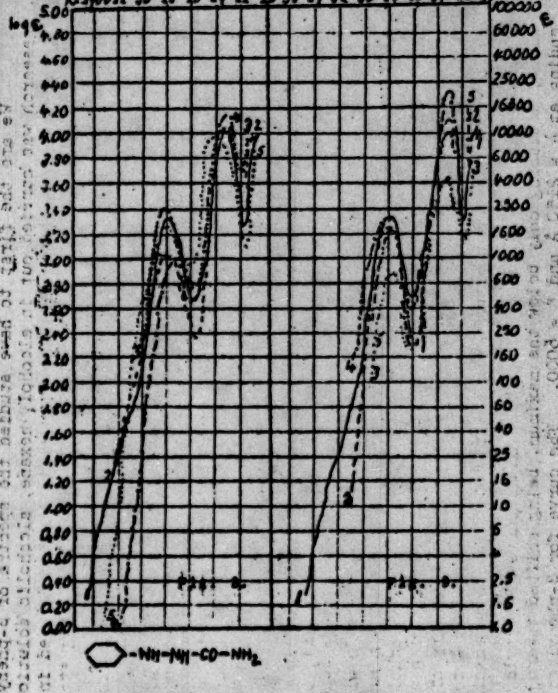



Fig. 8. 1-β-(m-tolyl)-semicarbazide in alcohol, from $10^{-1}$ to $5\cdot10^{-5}$ mol; 2-β-(m-tolyl)-semicarbazide in alcohol, $10^{-2}$ to $5\cdot10^{-5}$ mol, after standing overnight; 3-(· · ·) β-(m-tolyl)-semicarbazide in hexane from $5\cdot10^{-4}$ to $5\cdot10^{-5}$ mol; 4-(-·-) β-phenylsemicarbazide in alcohol from $10^{-1}$ to $5\cdot10^{-5}$ mol; 5-(· · ·) phenylhydrazine in alcohol, from $10^{-1}$ to $10^{-4}$ mol.

Fig. 9. 1-β-(m-tolyl)-semicarbazide in alcohol, $10^{-1}$ to $5\cdot10^{-5}$ mol; 2-β-(m-tolyl)-semicarbazide in alcohol, from $10^{-2}$ to $10^{-4}$ mol; + 100-molal HCl; 3-(· · ·) β-(m-tolyl)-semicarbazide in alcohol, from $10^{-4}$ to $5\cdot10^{-5}$ mol, + 100-molal HCl, after standing overnight; 4-(-·-) β-(m-tolyl)-semicarbazide in alcohol, from $5\cdot10^{-4}$ to $5\cdot10^{-5}$ mol, + 2-molal HCl; 5-(-··-) β-(m-tolyl)-semicarbazide in 36-molal HCl, from $5\cdot10^{-4}$ to $5\cdot10^{-5}$ mol.

after standing overnight does not coincide with the curve for phenylhydrazine in alcohol after standing for 15 hours (Fig. 6, Curves 3 and 6) either in intensity or in form or in the positions of the maxima, but resembles the phenylhydrazine curve, as was the case with β-acetylphenylhydrazine. Curve 2 (Fig. 6) for β-phenylsemicarbazide in hexane at a concentration of $5 \cdot 10^{-5}$ mol exhibits one $g_2$ band with a maximum at $\lambda$ = 2330 Å and $\varepsilon$ = 3000, which is shifted 25 Å farther toward the ultraviolet, being lower than the $g_2$ band in the alcoholic solution by a factor of 1.75. Owing to the difficulty of solution in hexane, we were unable to plot a complete curve.

TABLE 18

β-Phenylsemicarbazide in Alcohol, From $10^{-1}$ to $5 \cdot 10^{-5}$ Mol. (Fig. 6, Curve 1)

| λ | ε | λ | ε | λ | ε |
|---|---|---|---|---|---|
| 3270 | 1 | 2630 min. | 600 | 2290 | 10000 |
| 3110 | 10 | 2580 | 600 | 2240 | 4000 |
| 3000 | 100 | 2480 | 3200 | 2210 min. | 2000 |
| 2780 max. | 1000 | 2360 max | 14000 | 2180 | 2000 |
| 2690 | 1000 | 2320 | 14000 | 2130 | 6000 |

TABLE 19

β-Phenylsemicarbazide in Alcohol, From $10^{-2}$ to $5 \cdot 10^{-5}$ Mol, + 100-Molal HCl (Fig. 7, Curve 2)

| λ | ε | λ | ε | λ | ε |
|---|---|---|---|---|---|
| 3230 | 10 | 2710 | 1000 | 2360 max. | 12000 |
| 3080 | 35 | 2650 min. | 640 | 2330 | 12000 |
| 2880 | 1000 | 2570 | 640 | 2405 min. | 2000 |
| 2830 | 1400 | 2480 | 1600 | 2180 | 2000 |
| 2760 max. | 1400 | 2435 | 3000 | 2135 | 5000 |

β-Phenylsemicarbazide in Alcohol, From $10^{-2}$ to $5 \cdot 10^{-5}$ Mol, + 100-Molal HCl (Fig. 7. Curve 2)

The curve starts near the phenylhydrazine curve, at $\lambda$ = 3230 Å, $\varepsilon$ = 10, almost coinciding with the alcohol curve at $\lambda$ = 3050 Å and, rising upward, exhibits a maximum of the $g_1$ band at $\lambda$ = 2795 Å and $\varepsilon$ = 1400 that is shifted 60 Å toward the visible region compared to the alcohol curve and is 1.4 times as intense. The maximum of the $g_2$ band coincides with the latter's maximum, but is 1.15 times lower.

The absorption spectrum of β-phenylsemicarbazide in alcohol, from $5 \cdot 10^{-2}$ to $5 \cdot 10^{-5}$ mol, + 100-molal HCl, exhibited no changes after standing overnight.

β-Phenylsemicarbazide in 5-Molal HCl, from $5 \cdot 10^{-4}$ to $5 \cdot 10^{-5}$ Mol. (Fig.7,Curve 3)

The curve begins at $\lambda$ = 2950 Å and $\varepsilon$ = 200, being shifted 30 Å toward the visible region compared to the alcohol curve, and moves upward, exhibiting two phenylhydrazine bands: $g_1$ at $\lambda$ = 2780 Å and $\varepsilon$ = 1200, and $g_2$ at $\lambda$ = 2303 Å and $\varepsilon$ = 10,000, and ends at $\lambda$ = 2180 Å and $\varepsilon$ = 2600. The large excess of HCl causes no essential changes, the curve being merely somewhat shifted toward the ultraviolet. The band intensity of the absorption spectrum of β-phenylsemicarbazide in 5-molal HCl is very much like that of the spectrum of phenylhydrazine in alcohol + 100 molal HCl (Fig. 7, Curve 6).

β-Phenylsemicarbazide in alcohol plus 10-molal sodium alcoholate clouded and turned red as soon as the latter was added; hence, our research was conducted only in alcohol with 2 mols of sodium alcohol in solution: from $5 \cdot 10^{-4}$ to $5 \cdot 10^{-5}$ mol, + 2-molal $NaOC_2H_5$ (Table 21).

The absorption spectrum of β-phenylsemicarbazide also corresponds to the spectrum of the hydrazo form of phenylhydrazine, and its band intensity is very much like

TABLE 20

β-Phenylsemicarbazide in 5-Molal HCl, From $5 \cdot 10^{-4}$ to $5 \cdot 10^{-5}$ Mol. (Fig. 7, Curve 3)

| λ | ε | λ | ε | λ | ε |
|---|---|---|---|---|---|
| 2950 | 200 | 2645 min. | 320 | 2355 max. | 10000 |
| 2830 max. | 1200 | 2550 | 320 | 2270 | 10000 |
| 2780 | 1200 | 2435 | 3200 | 2180 | 2600 |

TABLE 21

β-Phenylsemicarbazide in Alcohol, From $5 \cdot 10^{-4}$ to $5 \cdot 10^{-5}$ Mol, + 2-Molal $NaOC_2H_5$ (Fig. 7, Curve 4)

| λ | ε | λ | ε | λ | ε |
|---|---|---|---|---|---|
| 2980 | 200 | 2730 | 2300 | 2390 max. | 20000 |
| 2850 max. | 4000 | 2610 min. | 800 | 2300 | 20000 |
| 2750 | 4000 | 2530 | 800 | 2240 | 10000 |

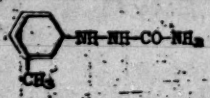
TABLE 22

| Items | $g_1$ λ | $g_1$ ε | $g_2$ λ | $g_2$ ε |
|---|---|---|---|---|
| β-Phenylsemicarbazide in alcohol | 2735 | 1000 | 2340 | 14000 |
| " in alcohol after standing overnight | 2785 | 8000 | 2340 | 14000 |
| β-Phenylsemicarbazide + 100 mols of HCl | 2795 | 1400 | 2345 | 12000 |
| " + 100 mols of HCl, after standing overnight | 2815 | 1400 | 2340 | 12000 |
| β-Phenylsemicarbazide in 5-molar HCl | 2780 | 1200 | 2303 | |
| " + 2 mols of $NaOC_2H_5$ | 2800 | 4000 | 2345 | 10000 |
| β-Acetylphenylhydrazine in alcohol | 2810 | 1000 | 2333 | 20000 |
| Phenylhydrazine in alcohol | 2828 | 1600 | 2410 | 9000 |

that of the spectrum of β-acetylphenylhydrazine. The intensity of the $g_1$ band changes after standing, growing 3 times as strong, and growing 1.4 times as strong when acted upon by acid; the addition of 2 mols of sodium alcoholate produces an exceptionally high increase. The intensity of the $g_2$ band does not change when the alcoholic solution is allowed to stand. It drops somewhat under the action of the acid, and is doubled under the action of the alkali.

Fig. 7 (curve 4) exhibits two more intense bands, $g_1$ with maximum at λ = 2800 Å and ε = 4000, and $g_2$ with maximum at λ = 2345 Å and ε = 20,000.

β-(m-Tolyl)-semicarbazide (m-Tolylhydrazide of Carbamic Acid, or Maretin)




We made a spectrographic analysis of β-(m-tolyl)-semicarbazide in alcohol, hexane, alcoholic solutions of hydrogen chloride, and sodium alcoholate.

β-(m-Tolyl)-semicarbazide in Hexane, Analyzed from $5 \cdot 10^{-4}$ to $5 \cdot 10^{-5}$ Mol (Fig. 8, Curve 3).

The curve starts close to the alcohol curve (Fig. 8, Curve 1), rising, and exhibiting a maximum of the $g_1$ band at λ = 2845 Å and ε = 2600; then, rising, it

exhibits the $g_2$ band at $\lambda$ = 2345 Å and $\varepsilon$ = 10,000; the curve comes to an end at $\lambda$ = = 2150 Å and $\varepsilon$ = 10,000 (Table 23).

β-(m-Tolyl)-semicarbazide in Alcohol, from $10^{-1}$ to $5 \cdot 10^{-5}$ (Fig.8, Curve 1)

The curve starts at $\lambda$ = 3465 Å and $\varepsilon$ = 2, and is shifted 105 Å toward the visible region with respect to the curve of phenylhydrazine in alcohol (Fig. 8, Curve 5); then, rising upward and displaced toward the longer wavelengths, it exhibits a maximum of the $g_1$ band at $\lambda$ = 2865 Å and $\varepsilon$ = 2000, and a maximum of the $g_2$ band at $\lambda$ = 2348 Å and $\varepsilon$ = 10,000. Compared to the $g_1$ and $g_2$ bands of phenylhydrazine in alcohol, the spectrum of β-(m-tolyl)-semicarbazide is shifted somewhat toward the ultraviolet (Table 24).

TABLE 23

β-(m-Tolyl)-semicarbazide in Hexane, from $5 \cdot 10^{-5}$ to $6 \cdot 10^{-5}$ Mol (Fig. 8, Curve 3).

| λ | ε | λ | ε | λ | ε |
|---|---|---|---|---|---|
| | | | | max. | |
| 3050 | 200 | 2665 | 600 | 2290 | 10000 |
| | | min. | | | |
| 2870 | 2600 | 2590 | 600 | 2230 | 5000 |
| max. | | | | min. | |
| 2820 | 2600 | 2510 | 2000 | 2200 | 5000 |
| 2710 | 1000 | 2400 | 10000 | 2150 | 10000 |
| | | max. | | | |

TABLE 24

β-(m-Tolyl)-semicarbazide in Alcohol, from $10^{-1}$ to $5 \cdot 10^{-5}$ Mol. (Fig. 8, Curve 1).

| λ | ε | λ | ε | λ | ε |
|---|---|---|---|---|---|
| 3465 | 2 | 2950 | 600 | 2380 | 10000 |
| | | | | max. | |
| 3425 | 3 | 2860 | 2000 | 2315 | 10000 |
| | | max. | | | |
| 3385 | 6 | 2790 | 2000 | 2270 | 5000 |
| 3360 | 8 | 2650 | 500 | 2220 | 2000 |
| | | min. | | min. | |
| 3280 | 16 | 2580 | 500 | 2195 | 2000 |
| 3060 | 100 | 2430 | 6000 | 2130 | 8000 |

TABLE 25

β-(m-Tolyl)-semicarbazide in alcohol, from $10^{-2}$ to $10^{-4}$ mol, + 100 Mols of HCl (Fig. 9, Curve 2)

| λ | ε | λ | ε | λ | ε |
|---|---|---|---|---|---|
| 3120 | 10 | 2865 | 1600 | 2350 | 12000 |
| | | max. | | max. | |
| 3080 | 20 | 2770 | 1600 | 2300 | 12000 |
| | | | | min. | |
| 3035 | 60 | 2660 | 600 | 2230 | 3200 |
| 3020 | 100 | 2630 | 400 | 2195 | 3200 |
| | | min. | | | |
| 2980 | 200 | 2580 | 400 | 2140 | 14000 |

TABLE 26

β-(m-Tolyl)-semicarbazide in Alcohol, from $10^{-3}$ to $5 \cdot 10^{-5}$ Mol, + 100 Mols of HCl, After Standing Overnight. (Fig. 9, Curve 3)

| λ | ε | λ | ε | λ | ε |
|---|---|---|---|---|---|
| | | | | max. | |
| 2970 | 100 | 2670 | 200 | 2320 | 4000 |
| | | min. | | | |
| 2850 | 700 | 2570 | 200 | 2210 | 1400 |
| max. | | | | min. | |
| 2750 | 700 | 2485 | 1000 | 2190 | 1400 |
| 2700 | 320 | 2380 | 4000 | 2180 | 6000 |
| | | max. | | | |

β-(m-Tolyl)-semicarbazide in Alcohol, from $10^{-2}$ to $5 \cdot 10^{-5}$ Mol, After Standing Overnight (Fig. 8, Curve 2).

The curve exhibits no essential changes, but the intensity of the $g_1$ band is halved. When we compare the curve of β-(m-tolyl)-semicarbazide with the curve of β-phenylsemicarbazide in alcohol (Fig. 8, Curves 1 and 4), we find that the intensity of the $g_1$ band is doubled and its maximum is shifted 90 Å toward the ultraviolet, the shift of band $g_2$ being almost within the limits of experimental error, though its intensity is increased by a factor of 1.4.

β-(m-Tolyl)-semicarbazide in Alcohol, from $10^{-2}$ to $10^{-4}$ Mol, + 100 Mols of HCl. (Fig. 9, Curve 2)

The curve begins at $\lambda$ = 3120 Å and $\varepsilon$ = 10, but is shifted 210 Å toward the ultraviolet as compared to the curve in alcohol; it rises upward, constantly approaching closer to the latter, and exhibits a maximum of the $g_1$ band at $\lambda$ = 2818 Å and $\varepsilon$ = 1600 and of the $g_2$ band at $\lambda$ = 2325 Å, and $\varepsilon$ = 12,000; it comes to an end at $\lambda$ = 2140 Å and $\varepsilon$ = 14,000 (Table 25).

β-(m-Tolyl)-semicarbazide in Alcohol, From $10^{-3}$ to $5 \cdot 10^{-5}$ Mol, + 100 Mols of HCl, After Standing Overnight (Fig. 9, Curve 3)

The curve exhibits two phenylhydrazine bands; $g_1$ at $\lambda$ = 2800 Å and $\varepsilon$ = 700, and $g_2$ at $\lambda$ = 2350 Å and $\varepsilon$ = 4000.

The maxima of the $g_1$ and $g_2$ bands are diminished by an approximate factor of 2.5, compared to the curve in alcohol and the curve in alcohol + 100 mols of HCl, recorded immediately after the latter's addition.

β-(m-Tolyl)-semicarbazide in 5 Mols of HCl, From $5 \cdot 10^{-4}$ to $5 \cdot 10^{-5}$ Mol. (Fig. 9, Curve 5).

The intensity of the $g_1$ band is the same as that of the curve for 100 mols of HCl (Fig. 9, Curve 2), but is shifted 30 Å toward the ultraviolet. The $g_2$ band is narrower and exhibits a maximum at $\lambda$ = 2330 Å and $\varepsilon$ = 20,000, its intensity being greater than that of the curve for the solution + 100 mols of HCl by a factor of approximately 1.6.

β-(m-Tolyl)-semicarbazide, From $5 \cdot 10^{-4}$ to $5 \cdot 10^{-5}$ Mol, + 2 Mols of $NaOC_2H_5$ (Fig 9, Curve 4; Table 28)

The curve begins at $\lambda$ = 3090 Å and $\varepsilon$ = 200, shifted 50 Å toward the visible region as compared to the alcohol curve; it rises and exhibits a maximum of the $g_1$ band at $\lambda$ = 2830 Å $\varepsilon$ = 2000 and of the $g_2$ band at $\lambda$ = 2325 Å, $\varepsilon$ = 10,000 and terminates at $\lambda$ = 2130 Å and $\varepsilon$ = 10,000. Compared to the alcohol curve (Fig. 9, curve 1), the $g_1$ band is wider, while the two $g_2$ bands coincide within the limits of experimental error (Table 29).

As with the acetyl group, when the $-CO-NH_2$ group is introduced at the beta position into phenylhydrazine and m-tolylhydrazine, it confers exceptional stability

TABLE 27

β-(m-Tolyl)-semicarbazide in 5-Molal HCl, from $5 \cdot 10^{-4}$ to $5 \cdot 10^{-5}$ Mol. (Fig. 9, Curve 5).

| λ | ε | λ | ε | λ | ε |
|---|---|---|---|---|---|
| 2980 | 200 | 2650 | 200 | 2270 | 20000 |
| | | min. | | | |
| 2925 | 500 | 2530 | 200 | 2235 | 3200 |
| | | | | min. | |
| 2820 | 1600 | 2440 | 3200 | 2205 | 3200 |
| max. | | | | | |
| 2755 | 1600 | 2350 | 20000 | 2105 | 10000 |
| | | max. | | | |
| 2715 | 1000 | 2310 | 20000 | 2150 | 16000 |

TABLE 28

β-(m-Tolyl)-semicarbazide, in alcohol, from $5 \cdot 10^{-4}$ to $5 \cdot 10^{-5}$ mol + 2 mols $NaOC_2H_5$ (Fig. 9, Curve 4)

| λ | ε | λ | ε | λ | ε |
|---|---|---|---|---|---|
| | | | | max. | |
| 3090 | 200 | 2620 | 260 | 2300 | 10000 |
| | | minimum | | | |
| 2880 | 2000 | 2665 | 260 | 2330 | 2600 |
| maximum | | | | minimum | |
| 2780 | 2000 | 2510 | 1000 | 2190 | 2600 |
| 2720 | 1000 | 2530 | 10000 | 2130 | 10000 |
| | | max. | | | |

upon the hydrazo structure of the phenylhydrazine. The variability of solutions in alcohol and in solutions of hydrogen chloride upon standing partially indicates the presence of a diazo structure or of other changes. A large quantity of sodium alcoholate causes cloudiness and coloring of the solutions; in a bimolal solution of sodium alcoholate, the absorption maxima are increased and are somewhat different, owing to the possibility of interaction between the sodium alcoholate and the carbonyl group or directly with the alpha nitrogen atom.

TABLE 29

| Items | $g_1$ | | $g_2$ | |
|---|---|---|---|---|
| | λ | ε | λ | ε |
| β-(m-Tolyl)-semicarbazide in alcohol..... | 2825 | 2000 | 2348 | 10000 |
| " in alcohol after standing overnight ..... | 2830 | 1000 | 2340 | 10000 |
| β-(m-Tolyl)-semicarbazide in hexane ..... | 2945 | 2600 | 2345 | 10000 |
| " + 100 mols of HCl..... | 2813 | 1600 | 2325 | 12000 |
| " + 100 mols of HCl after standing overnight.... | 2800 | 700 | 2350 | 4000 |
| β-(m-Tolyl)-semicarbazide in 5-molar HCl..... | 2798 | 1600 | 2330 | 20000 |
| + 2 mols of $NaOC_2H_5$..... | 2830 | 2000 | 2325 | 10000 |
| β-Phenylsemicarbazide in alcohol..... | 2735 | 1000 | 2340 | 14000 |
| Phenylhydrazine in alcohol ..... | 2828 | 1600 | 2410 | 9000 |

## General Consideration of the Absorption Spectra of the β-Acyl Derivatives of Phenylhydrazine

The spectrographic investigations of N.A. Valyashko and V.I.Bliznyukov [16] have established two structures for phenylhydrazine: the hydrazo and the diazo structures, which are in dynamic equilibrium with each other:

$$C_6H_5\text{-}NH\text{-}NH_2 \rightleftharpoons C_6H_5\ \overline{N}\text{-}\overset{+}{N}H_3,$$

the first being characterized by two absorption bands, and the second by one wide band (Fig. 1, Curves 5 and 6).

The spectra of the beta acyl derivatives of phenylhydrazine were compared with these phenylhydrazine spectra.

Comparison of the absorption spectra of phenylhydrazine and of the beta acyl derivatives shows that the beta acyl derivatives correspond to a hydrazo structure of phenylhydrazine in so far as their number of bands and their absorption intensity are concerned.

The existence of a diazo structure in these compounds is not clearly exhibited in the spectra, as has been noted above. But it may be assumed in some degree, in view of the slight change in the spectra of both the alcoholic and neutral solutions as well as those with HCl present, upon standing. This causes the $g_1$ band to become more intense and narrower, indicating a certain shift in the equilibrium toward the hydrazo structure.

The effect of the acetyl group – $COCH_3$ – when in the beta position in acetylphenylhydrazine upon the first band, $g_1$, is a slight displacement of the band toward the shorter wave-lengths, while the absorption intensity is diminished (I).

TABLE 30

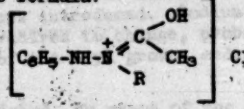
| Items | $g_1$ | | b | | $g_2$ | |
|---|---|---|---|---|---|---|
| | λ | ε | λ | ε | λ | ε |
| In alcoholic solutions of phenylhydrazine | | | | | | |
| Diazo structure $C_6H_5-\overset{+}{N}-NH_3$ ..... | | | 2725 | 13333 | | |
| Hydrazo structure $C_6H_5-NH-NH_2$ ..... | 2828 | 1600 | | | 2410 | 9000 |
| Phenylhydrazine in a 5-molal solution of HCl..... | 2760 | 1200 | | | 2295 | 12000 |
| I. β-Acetylphenylhydrazine: $C_6H_5NH-NH-COCH_3$..... | 2810 | 1000 | | | 2333 | 10000 |
| II. β,β-Methylacetylphenylhydrazine: $C_6H_5-NH-N(CH_3)(COCH_3)$ ..... | 2830 | 4000 | | | 2320 | 20000 |
| III. β-Phenylsemicarbazide of carbamic acid: $C_6H_5-NH-NH-CO-NH_2$ ..... | 2735 | 1000 | | | 2340 | 14000 |
| IV. β-(m-Tolyl)-hydrazide of carbamic acid: $CH_3-C_6H_4-NH-NH-CO-NH_2$ ... | 2825 | 2000 | | | 2348 | 10000 |
| V. Analine (according to Biquard's curve)..... | 2845 | 1550 | | | 2330 | 8650 |

Introducing a $CH_3$ group into β-acetylphenylhydrazine in place of another beta hydrogen atom (II) displaces this band again toward the longer wavelengths, the $g_1$ band being again located at the same wavelengths as in unsubstituted phenylhydrazine, but the band intensity is 2.5 times as high. Introducing the carbamic acid group – $CO-NH_2$ – at the beta position shifts the $g_1$ band still more toward the shorter wavelengths and lowers the intensity of absorption of β-phenylhydrazine (III); in β-(m-tolyl)-hydrazine (IV) no shift takes place, while the absorption intensity of the $g_1$ band is doubled. All substitutions are reflected in the second $g_2$ band of phenylhydrazine by a shift toward the shorter wavelengths and an increase in the absorption intensity, of as much as 1.4 times in III and 1.6 times in II.

According to the researches of N.Valyashko and V.Bliznyukov [16], the absorption spectrum of the hydrazo form of phenylhydrazine greatly resembles the absorption spectrum of aniline, which likewise has two absorption bands, as is shown by the data listed in Table 30. The resemblance with the aniline spectra persists in the 5-molal alcohol solution of HCl, with which phenylhydrazine forms the salt $[C_6H_5-NH-\overset{+}{N}H_3]Cl^-$, both of the bands being shifted toward the shorter wavelengths. These figures indicate that, in phenylhydrazine and in its salt, as well as in its beta acyl derivatives we have investigated, the absorption spectrum is chiefly due to the reaction of the alpha NH group with the benzene ring. The role played by the beta $NH_2$ group of the phenylhydrazine in the constitution of the absorption spectrum is a secondary one, being manifested by relatively slight displacements and more appreciable changes in intensity, as has been shown in the formation of the salt and of the beta derivatives. The comparatively slight effect of alcoholic solutions of HCl upon the spectrum of the beta acyl derivatives of phenylhydrazine may be due to the fact that the entering acyl groups cause a diminution in the basicity of the

nitrogen atom in the salt-forming beta amino group, as is generally the case in acid amides.

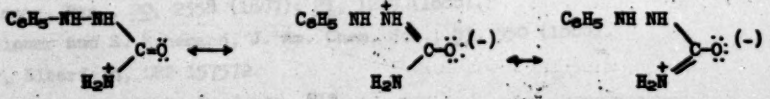
The most probable structre of the salt [17], say, for beta acylated phenylhydrazines, is given by the formula:



again exhibiting a structural change at the beta nitrogen. This is paralleled by a change in the physiological action of phenylhydrazine. Phenylhydrazine, β-acetylphenylhydrazine, and β,β-methylacetylphenylhydrazine, like aniline, act as powerful antipyretica, as well as toxins that break down the coloring matter in the blood (hemoglobin). Introducing acyl and alkyl groups at the beta position in phenylhydrazine diminishes the toxicity, but the substances still remain blood poisons. Introducing a carbamic group - $CO-NH_2$ - at the beta position diminishes the toxic action of phenylhydrazine upon the blood extremely effectively, although it does not eliminate it entirely, the resulting phenylhydrazides of carbamic acid possessing strong antipyretic properties and being used therapeutically under the trade names of cryogenin and maretin.

The difference between more and less toxic preparations is not clearly manifest in the absorption spectra of the beta acyl derivatives of phenylhydrazine that we have investigated. All that can be said is that introducing the acyl or carbamic group at the beta position shifts the absorption bands toward the shorter wavelengths, indicating that the molecules become more stable and less reactive. This effect is due to the fact that the acetyl group diminishes the mobility of the beta atom's electrons, owing to the properties of a C=O group to attract electrons to the oxygen, as well as owing to the possibility of resonance, [18]:

The phenomenon of resonance will be even more markedly manifest when a carbamic group is introduced into the phenylhydrazine, forming a urea group (carbamide), characterized by resonance with a high resonance energy:



It is possible that the large part played by the beta amino group in the resonance of the beta carbamic derivatives of phenylhydrazine is responsible for the considerable diminution of their toxicity. Elucidation of these problems requires more precise spectrographic analysis.

## SUMMARY

1. The syntheses of β-acetylphenylhydrazine (hydracetin), β,β-methylacetylphenylhydrazine, β-phenylsemicarbazide (cryogenin), and β-(m-tolyl)-semicarbazide (maretin) have been worked out.

2. The absorption spectra of the foregoing beta acyl-substituted phenylhydrazines

have been investigated in hexane, alcohol, sodium alcoholate, and in the presence of hydrogen chloride.

3. It has been found that the absorption spectra of these compounds in alcoholic solutions of hydrogen chloride change but little, owing to the lowered basicity of the beta nitrogen in the acyl groups introduced. Sodium alcoholate causes the absorption spectra of the beta acyl derivatives to change, probably owing to the reaction of the alcoholate with the carbonyl of the acyl groups and, perhaps, with the alpha nitrogen atom directly.

4. It has been established, by means of the absorption spectra, that all the beta acyl derivatives of phenylhydrazine investigated correspond to a hydrazo structure for the phenylhydrazine, with, perhaps, merely a slight percentage of the diazo structure.

5. Introducing acyl groups at the beta amino group of phenylhydrazine shifts the absorption spectrum to the shorter wavelengths and reduces toxicity: slightly in the beta acyl derivatives of phenylhydrazine and more so in the beta carbamic derivatives.

6. In their hydrazo structure, the beta acyl derivatives of phenylhydrazine border on antipyrine and pyramidon.

In the latter, the diminution of the toxicity of the phenylhydrazine group is due to the closing of the pyrazolone ring, according to N.A.Valyashko and V.I.Bliznyukov [18].

In ... β-acetylphenylhydrazine (hydracetin) and in β-phenylhydrazine and the β-(m-tolyl)-hydrazide of carbamic acid (cryogenin and maretin, respectively), the toxicity of the phenylhydrazine group is reduced as follows: very slightly in the first, and more so in the latter two, owing to the entrance of the beta nitrogen atom into acetamide resonance and of another atom into carbamide resonance, with higher resonance energy.

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# THE PHOTOCHEMICAL REACTIONS OF ORGANOMETALLIC COMPOUNDS OF MERCURY IN SOLUTIONS

## V. THE PHOTOCHEMICAL REACTIONS OF α-DINAPHTHYLMERCURY

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In our investigation of the catalytic decomposition of α-dinaphthylmercury [1] we noted a peculiarity of this compound, compared to diphenylmercury. The latter breaks down when acted upon by metallic catalysts (Pt, Ni, Ag, etc.), liberating mercury and dimerizing the phenylradicals to diphenyl. The naphthyl radicals are not dimerized to dinaphthyl, but react with each other, redistributing the hydrogen and giving rise to naphthalene and an insoluble carbon residue.

We were interested in exploring the photochemical reactions of α-dinaphthylmercury in order to compare them with the photoreactions of diphenylmercury [2].

When α-dinaphthylmercury is irradiated by ultraviolet light in chloroform, tetrachloroethane, or dichloroethane, α-naphthylmercury chloride is formed quantitatively. The naphthyl radical releases hydrogen and is converted into naphthalene.

With chloroform, for example, the reaction is as follows:

$$(C_{10}H_7)_2Hg + \underline{h\nu} \longrightarrow C_{10}H_7Hg^{\cdot} + C_{10}H_7^{\cdot}$$

$$C_{10}H_7Hg^{\cdot} + CHCl_3 \longrightarrow C_{10}H_7HgCl + {}^{\cdot}CHCl_2$$

$$C_{10}H_7^{\cdot} + CHCl_3 \longrightarrow C_{10}H_8 + {}^{\cdot}CCl_3$$

$$2\cdot CCl_3 \longrightarrow Cl_3C{-}CCl_3$$

The reaction with ethyl bromide is similar: naphthylmercury bromide is evolved quantitatively, and naphthalene is formed.

The reaction with methyl iodide is more thoroughgoing. In this reaction mercuric iodide is produced as well as naphthylmercury iodide. A photoreaction with ethyl iodide yielded only mercuric iodide. In both instances, the detached naphthyl radical was converted into naphthalene.

The photoreaction of α-dinaphthylmercury with alcohols is extremely difficult owing to the extremely poor solubility of dinaphthylmercury in alcohols.

Irradiating α-dinaphthylmercury and methanol yielded no results at all. When the former was irradiated for a long time with isoamyl alcohol, the photoreaction resulted in the liberation of mercury and the formation of naphthalene. Thus, the

foregoing reactions are entirely similar to the respective reactions with diphenylmercury.

The difference between the behavior of the naphthyl and phenyl radicals made itself manifest in the photoreactions with carbon tetrachloride. The phenyl radical first detaches an atom of hydrogen from the solvent, producing benzene, and chlorobenzene is formed in the carbon tetrachloride solution as a result of the addition of a chlorine atom to the phenyl radical.

The photoreaction of α-dinaphthylmercury with carbon tetrachloride produced a quantitative yield of naphthylmercury chloride, plus naphthalene, hexachloroethane, and an amorphous, non-crystallizing residue. The reaction probably followed this course:

$$(C_{10}H_7)_2Hg + h\nu \longrightarrow C_{10}H_7Hg^{\cdot} + C_{10}H_7^{\cdot}$$

$$C_{10}H_7Hg^{\cdot} + CCl_4 \longrightarrow C_{10}H_7HgCl + {}^{\cdot}CCl_3$$

$$2{}^{\cdot}CCl_3 \longrightarrow Cl_3C - CCl_3$$

$$2C_{10}H_7^{\cdot} \longrightarrow C_{10}H_8 + (C_{10}H_6)_x$$

Hence, the naphthyl radical does not react with the carbon tetrachloride; here, as in the catalytic decomposition of α-dinaphthylmercury, the hydrogen is redistributed among the naphthyl radicals.

It is noteworthy that the naphthyl radical produced in the thermal decomposition of α-naphthoyl peroxide to carbon tetrachloride [3] reacts with the latter to yield α-chloronaphthalene and hexachloroethane.

## EXPERIMENTAL

### α-Dinaphthylmercury and Carbon Tetrachloride

1 g of α-dinaphthylmercury in 15 ml of carbon tetrachloride was irradiated for 20 hours. The solution turned brown. The precipitate was filtered out and recrystallized from benzene; m.p. 189° without depression when mixed with pure α-naphthylmercury chloride; weight 0.74 g (93% of the theoretical).

The filtrate was distilled with steam; after the carbon tetrachloride had been driven off, a white substance congealed in the condenser; it proved to be naphthalene, with a m.p. of 80°, exhibiting no depression when mixed with a pure preparation and yielding a picrate with a m.p. of 150°. The distillation residue was a tarry mass. The carbon tetrachloride was separated from the water and distilled over a water bath; the residue contained hexachloroethane, with a m.p. of 187° (in a sealed capillary), exhibiting no depression when mixed with pure hexachloroethane.

### α-Dinaphthylmercury and Chloroform

1.5 g of α-dinaphthylmercury in 20 ml of chloroform was irradiated for 20 hours. The precipitate was filtered out and recrystallized from benzene; it proved to be α-naphthylmercury chloride, with a m.p. of 187°, exhibiting no depression when mixed with the pure substance; the weight was 0.65 g. The filtrate was distilled with steam; 0.28 g of naphthalene, with a m.p. of 80°, which exhibited no depression when mixed with the pure substance, congealed in the condenser; the picrate had a m.p. of 150°. Hexachloroethane was extracted as in the previous experiment (m.p. 187° in a sealed capillary). The residue left after steam distillation was recrystallized from benzene; it proved to be α-naphthylmercury chloride, with a m.p. of 189°, exhibiting no depression when mixed with the pure substance; its weight was 0.5 g. Hence, a total of 1.15 g of α-naphthylmercury chloride was recovered, or 96% of the theoretical.

## α-Dinaphthylmercury and Tetrachloroethane

1 g of α-dinaphthylmercury in 15 ml of tetrachloroethane was irradiated for 35 hours. The solution turned dark brown, but no precipitate was formed. The solution was distilled with steam. A solid substance congealed in the condenser; it proved to be naphthalene, with a m.p. of 80° (after sublimation), which exhibited no depression when mixed with the pure substance. The residue left after steam distillation was recrystallized from benzene; the weight was 0.79 g (or 93% of the theoretical) of a substance with a m.p. of 187°, which exhibited no depression when mixed with pure α-naphthylmercury chloride.

## α-Dinaphthylmercury and 1,2-Dichloroethane

1 g of α-dinaphthylmercury in 15 ml of 1,2-dichloroethane was irradiated for 30 hours. The solution turned brown. A small quantity of metallic mercury separated out. The precipitate, weighing 0.15 g, was filtered out and recrystallized from benzene; its m.p. was 189°, and it exhibited no depression when mixed with pure α-naphthylmercury chloride. The solvent was driven off from the filtrate, and the residue was distilled with steam, yielding naphthalene; the latter weighed 0.18 g and had a m.p. of 80°, without any depression when mixed with the pure substance. The mass that did not distil over with the steam was recrystallized from benzene; it had a m.p. of 189°, without any depression when mixed with pure α-naphthylmercury chloride, and it weighed 0.6 g. Hence, a total of 0.75 g, or 95% of the theoretical, of α-naphthylmercury-chloride was recovered.

## α-Dinaphthylmercury and Ethyl Bromide

0.3 g of α-dinaphthylmercury chloride in 8 ml of ethyl bromide was irradiated for 15 hours. No gas was evolved during the reaction. The bottom of the test tube had a small amount of mercury. The ethyl bromide was driven off, and the residue was distilled with steam; this yielded naphthalene with a m.p. of 80°, which exhibited no depression when mixed with the pure substance. The residue left after steam distillation was α-naphthylmercury bromide, weighing 0.25 g (93% of the theoretical); it had a m.p. of 202° after recrystallization from acetone and exhibited no depression when mixed with pure α-naphthylmercury bromide.

## α-Dinaphthylmercury and Methyl Iodide

1 g of α-dinaphthylmercury in 15 ml of methyl iodide was irradiated for 24 hours. The solution turned brown, but no precipitate was formed. The methyl iodide was driven off, and the residue was distilled with steam. A substance with the color of iodine congealed in the condenser; sublimation over zinc dust yielded naphthalene with a m.p. of 80°, exhibiting no depression with the pure substance. The residue left after steam distillation weighed 0.95 g, of which 0.18 g (18% of the theoretical) was accounted for by red mercuric iodide, which was separated from the bulk of the residue by dissolving it in potassium iodide; the remainder of 0.77 g (77% of the theoretical) was recrystallized from a benzene-acetone mixture; it had a m.p. of 185° and exhibited no depression when mixed with pure α-naphthylmercury iodide.

## α-Dinaphthylmercury and Ethyl Iodide

1 g of α-dinaphthylmercury in 15 ml of ethyl iodide was irradiated for 15 hours. The solution turned a dark color, owing to the iodine evolved. The red mercuric iodide was filtered out, yielding 0.25 g. The ethyl iodide was driven off over a water bath, together with part of the iodine. The residue was distilled with steam. Naphthalene, colored with iodine, congealed in the condenser; sublimation over zinc dust yielded 0.1 g of naphthalene with a m.p. of 80°, exhibiting no depression when mixed with the pure substance. The residue left after steam distillation

proved to be red mercuric iodide, which dissolved completely in potassium iodide after having been washed with benzene; its weight was 0.7 g. The total mercuric iodide recovered was 0.95 g, or 95% of the theoretical.

### α-Dinaphthylmercury and Isoamyl Alcohol

1 g of α-dinaphthylmercury in 20 ml of isoamylalcohol was irradiated for a month and a half. The solution was slightly colored. The precipitate was filtered out. The unreacted α-dinaphthylmercury was extracted with hot dichloroethane, the residue containing 0.3 g of mercury, or 68% of the theoretical. Amyl alcohol was driven off from the filtrate, and the residue was distilled with steam. This yielded 0.15 g of naphthalene with a m.p. of 80°, exhibiting no depression when mixed with the pure product.

### α-Dinaphthylmercury and Methanol

0.5 g of α-dinaphthylmercury in 10 ml of methanol was irradiated for 2 months; traces of mercury were found, but the α-dinaphthylmercury remained unchanged.

## SUMMARY

1. When α-dinaphthylmercury is irradiated with ultraviolet light in $CHCl_3$, $C_2H_2Cl_4$, and $C_2H_4Cl_2$, a quantitative yield of naphthylmercury chloride and naphthalene is produced.

2. When α-dinaphthylmercury is irradiated with carbon tetrachloride, napthylmercury chloride and naphthalene are again produced as the result of the redistribution of the hydrogen between the naphthyl radicals.

3. The photoreaction of dinaphthylmercury with ethyl bromide yields naphthylmercury bromide and naphthalene.

4. The photoreaction of dinaphthylmercury with methyl iodide yields naphthylmercury iodide, mercuric iodide, and naphthalene; its photoreaction with ethyl iodide yields mercuric iodide and naphthalene.

5. The photoreaction of dinaphthylmercury with amyl alcohol yields naphthalene and mercury.

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# THE SULFONATION AND SULFO ACIDS OF ACIDOPHOBIC COMPOUNDS

## XI. USE OF THE LIXIVIATION METHOD TO INVESTIGATE THE PRODUCTS OF THE SULFONATION OF PYRROLE

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It has been demonstrated in the paper by Terentyev and Yanovskaya [1] that pyrrole is sulfonated by pyridine sulfotrioxide, yielding 90% of a monosulfonic acid. When sulfopyrrole is oxidized by a chromic acid mixture, maleinimide is recovered. This enables us to conclude that the sulfo group entered the pyrrole at the beta position. Methyl- and phenyl-substituted pyrroles, which have a free alpha position, behave similarly. A more detailed study of the reaction products of N-aryl-substituted pyrroles, on which we shall have occasion to report at length in one of our subsequent papers, indicated, however, that β-isomers are also formed in appreciable quantities. This compelled us to return to a study of the reaction products of pyridine sulfotrioxide with pyrrole itself.

To effect better identification of the α-sulfo acid, we synthesized the acid chloride and the anilide of pyrrolesulfonic-(2) acid. The acid chloride is formed by the reaction of the sodium sulfonate with phosphorus pentachloride, but it cannot be isolated in the pure state. Even in ether solution it turns black rapidly, within the course of a few minutes, evolving hydrogen chloride and turning into a black tar. When the freshly prepared acid chloride is treated with aniline, it yields the anilide: crystals with a m.p. of 142°. We were unable to isolate the amide in the pure state. It is apparent than the anilide and similar derivatives may, on the whole, be employed in the determination and identification of only the principal reaction product: the α-sulfo acid, and that the problem of the presence or absence of the β-sulfo-acid cannot be decided. Moreover, neither this latter isomer nor any of its derivatives has been synthesized up to the present time. We therefore resolved to employ the method of solubility and lixiviation [2] in our research on the products of the sulfonation of pyrrole. The solubility of the pure substance in a suitable solvent at a given temperature is a numerical property of the substance in question. If an unknown isomer does not change the percentage of the substance in a saturated solution when it is agitated with this solution, the unknown isomer is identical with the standard. And, conversely, if the sample under test has an appreciable percentage of another isomer, the percentages of the substances in solution ought to increase when the former is agitated with a saturated solution of the known isomer.

Our research fell into two stages: synthesis of the pure barium salt of pyrrolesulfonic-(2) acid, and the investigation of the barium salts obtained in the

sulfonation of pyrrole in a solution of the barium salt of a pure preparation of the α-sulfo acid. The first operation was performed as follows: We sulfonated the pyrrole by a method previously developed by us. The sulfo mass was separated from the sulfuric acid by the usual treatment with barium carbonate. After recrystallization from a water-alcohol mixture, the salt was dried and analyzed. Its barium content was that of a pyrrole monosulfonic acid. The purity of the standard barium salt of pyrrole-sulfonic-(2) acid was found by the stability of solubility of a sample of the salt during fourfold lixiviation. The solvent used was a mixture of methanol (2 parts by volume); the thermostat was set at 26°. At the same time, the time required for achieving saturation was established.

The second operation – analyzing the percentage of the β-isomer in the product of sulfonating the pyrrole – was performed as follows: The sulfo mass resulting from sulfonation of the pyrrole by pyridine sulfotrioxide at 100° was treated with barium carbonate. The precipitate was filtered out and washed with hot water. The filtrate was evaporated to dryness over a water bath and washed with ether to eliminate a small quantity of pyrrole tarring products. A weighed batch of the resulting unknown salt was placed in a saturated methanol-water solution (at 26°) with the bottom phase consisting of the barium salt of the α-isomer (tested as stated above). After having been agitated in a thermostat for three hours, a sample was taken. It was found that the percentage of barium in the solution remained unchanged within the limits of experimental error.

Thus, our investigation has shown that the sulfonation of pyrrole results in a practically quantitative yield (93% of the theoretical) of the α-isomer of monosulfopyrrole, with no detectable traces of the beta isomer and disulfo acids.

## EXPERIMENTAL

Anilide of pyrrolesulfonic-(2) acid. The barium salt of pyrrolesulfonic-(2)-acid, prepared by the method developed previously [1], was converted into the sodium salt by treatment with soda. The carefully dried sodium salt was comminuted with an excess of phosphorus pentachloride. The mixture was transferred to a flask and heated until the contents were completely melted; the latter were then dissolved in carbon tetrachloride. The solution was washed several times with cold water. Evaporation of the solvent left the acid chloride with a characteristic odor. After a few minutes the moist acid chloride decomposes, liberating hydrogen chloride and turning into a black mass. We were unable to synthesize the amide by the usual treatment with ammonia. The anilide was prepared by treating the acid chloride with an excess of aniline and was then extracted with ether. 1.5 g of the sodium salt yielded about 0.6 g of the anilide. Recrystallized from benzene, it fuses at 142°. It is readily soluble in alcohol and less so in ether.

3.492 mg substance: 0.398 ml $N_2$ (24°, 744 mm).
5.834 mg substance: 0.651 ml $N_2$ (24°, 744 mm).
Found %: N 12.79, 12.38.
$C_{10}H_{10}O_2N_2S$. Computed %: N 12.61.

Determination of the barium salts was accomplished by titration with soda by the Chalmers and Rigby method [3]. A weighed portion of the barium salt was dissolved in 10 ml of freshly boiled water and 7-8 ml of methanol. The solution was protected against carbon dioxide by a tube filled with soda lime. After it had cooled, it was titrated with decinormal soda in the presence of phenolphthalein. The appearance of a permanent pink color was easily observed against the white precipitate of barium carbonate.

Preparation of a sample of the barium salt of pyrrolesulfonic-(2) acid was

accomplished by triple recrystallization of the product obtained by sulfonating the (synthetic) pyrrole with pyridine sulfotrioxide (cf below). After it had been dried it was analyzed.

0.2032 g substance: consumed 9.44 ml 0.1 N $Na_2CO_3$.
0.2010 g substance: consumed 9.32 ml 0.1 N $Na_2CO_3$.
Found %: Ba 31.91, 31.84.
$C_4H_4O_3NSBa_{1/2}$. Computed %: Ba 31.98.

Checking the purity of the barium salt by lixiviation. 35 ml of a water-alcohol mixture consisting of 2 parts by volume of methanol and 3 parts by volume of water was added to a weighed quantity (1.627 g) of the previously analyzed salt in a wide test tube. The solution was saturated by agitation in a water thermostat at 26° ± 0.4°. It had been established in preliminary experiments that no more than 2 hours was needed for saturation. After three hours, the test tube was returned to the vertical position in the thermostat to enable the precipitate to settle out. Two 10-ml samples of the filtered solution were taken for analysis. 20 ml of the same water-alcohol mixture as that specified above was then added to the precipitate remaining in the test tube. The process of saturation was repeated, after which the same samples were taken for analysis. This lixiviation procedure was repeated four times. The bottom phase was always left behind. The solubility remained unchanged throughout all these operations.

Analysis of the pyrrole sulfonation product. The initial pyrrole was prepared by the destructive distillation of ammonium saccharate. B.p. 130°; $d_4^{20}$ 0.9658; $n_D^{20}$ 1.5096. The pyridine sulfotrioxide was prepared from sulfuric anhydride and pyridine dissolved in dichloroethane; it was carefully washed with pure dichloroethane and desiccated in a drying cabinet at 100°.

| Sample No. | Ml. of 0.1N $Na_2CO_3$ required for 10 ml of solution |
|---|---|
| 1 | 5.50, 5.52 |
| 2 | 5.49 |
| 3 | 5.50 |
| 4 | 5.49, 5.50 |
| Average | 5.50 ml. |

1.34 g of pyrrole, 9.54 g of pyridine sulfotrioxide (molar ratio 1:3), and 10 ml of dichloroethane were heated to 100° for 10 hours in a sealed tube. The dichloroethane solution was decanted from the darkened fused sulfo mass. The sulfo mass was dissolved in water and treated, while boiling, with a suspension of barium carbonate. The precipitate was filtered out and carefully washed with hot water. The filtrate was evaporated to dryness and washed with ether to remove tarry impurities. This yielded 8 g of the barium salt, corresponding to a yield of approximately 93% of the theoretical. A weighed portion of the salt (0.0621 g), without further purification, was placed in 35 ml of a saturated solution of barium pyrrolesulfonate-(2) (bottom phase) in a 2:3 water-alcohol medium. Two samples were taken for analysis after the mixture had been agitated in a thermostat at 26° for 3 hours.

10 ml of the solution required 5.52 ml of 0.1 N $Na_2CO_3$.
10 ml of the solution required 5.50 ml of 0.1 N $Na_2CO_3$

These titration figures correspond with those obtained for the pure barium pyrrolesulfonate-(2).

## SUMMARY

Sulfonating pyrrole with pyridine sulfotrioxide yields only one isomer: pyrrolesulfonic-(2) acid. This was proved by the fact that adding the barium salt isolated from the reaction product to a saturated water-alcohol solution of pure barium

pyrrolesulfonate-(2) does not affect the solubility of the latter.

A quantitative method has been developed for determining barium salts of sulfo acids by titration with a soda solution against phenolphthalein.

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# THE COLOR OF ORGANIC DYESTUFFS AND THE PLANARITY OF THEIR MOLECULES. II

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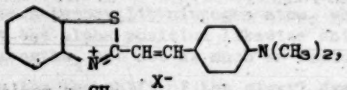
In our previous report [1] we showed that the steric hindrances that interfere with the planar structure of the molecules of symmetrical cyanine dyes produce a displacement of their absorption maxima toward the red end of the spectrum and a decrease in the absorption intensity.

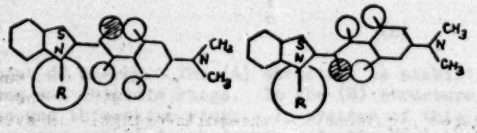
This rule applies only to symmetrical dyes or, more precisely, only to dyestuffs whose fundamental resonance structures differ but slightly in energy. Dyestuffs of quite asymmetrical structure may behave differently. Interference with the planarity of their molecules may shift their absorption bands toward the short-wave end of the spectrum.

Styryl dyestuffs:

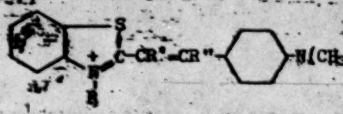


are examples of this kind of dyestuff. If we introduce a substituent at the methyl group of this compound that prevents the coplanarity of the thiazole and benzene rings, its absorption band will be shifted toward the violet end of the spectrum.

The drawing below illustrates the structure of the cation of a styryl dyestuff with two spatial configurations: cis and trans. We see that substituting a radical for the hydrogen atom at the beta position (shaded in the diagram) may rupture coplanarity, inasmuch as there is not enough room for locating the radical in the same plane as the benzene ring.



The following table gives the absorption maxima and the molecular extinctions for a number of styryls synthesized by us, with the following general formula:

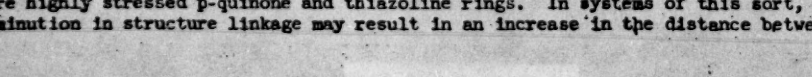


| Preparation | R | R' | R" | λmax in mμ | ε max·10⁻⁴ |
|---|---|---|---|---|---|
| I | $C_6H_5$ | H | H | 546 | 6.2 |
| II | $C_6H_5$ | $CH_3$ | H | 508 | 2.4 |
| III | $C_6H_5$ | $C_2H_5$ | H | 510 | 2.6 |
| IV | $C_6H_5$ | $C_6H_5$ | H | 540 | 3.5 |
| V | $C_2H_5$ | H | H | 530 | 11.0 |
| VI | $C_2H_5$ | $CH_3$ | H | 481 | 6.2 |
| VII | $C_2H_5$ | $C_2H_5$ | H | 482 | |
| VIII | $C_2H_5$ | $C_6H_5$ | H | 508 | 2.3 |
| IX | $C_6H_5$ | H | $CH_3$ | 538 | 2.2 |
| X | $C_6H_5$ | H | $C_6H_5$ | 550 | 1.3 |
| XI | $C_2H_5$ | H | $CH_3$ | 518 | 2.1 |

The following conclusions may be drawn from inspection of this table. Replacing a beta hydrogen atom by an alkyl group causes a marked shift of the absorption maximum toward the shorter wavelengths and a diminution in absorption intensity (II and III). A phenyl group has the same effect, though not as strongly. A hypsochromic displacement occurs no matter what radical, aliphatic or aromatic (VI-VIII), is attached to the heterocyclic nitrogen atom, which agrees with the drawing. Finally, radicals at the alpha position likewise shift the absorption maximum toward the shorter wavelengths, but not as much as radicals at the beta position.

The reason for the shift of the styryl dyestuffs' absorption maxima by the introduction of hydrocarbon radicals into their chromophores is apparently the same as in the case of the symmetrical carbocyanines described by us previously. Bulky substituents disturb the planar state of the molecule, diminish the linking of the resonance structures, and change the nature of the absorption. The styryl dyes differ from the carbocyanines, however, in that they exhibit a hypsochromic rather t than a bathychromic displacement of the absorption band.

The principal resonance structures of a styryl dye:



(A) (B)

are far from equivalent in point of energy. The (A) structure is stabilized by the resonance energy of the benzene and thiazole rings. In the (B) structure we see the more highly stressed p-quinone and thiazoline rings. In systems of this sort, the diminution in structure linkage may result in an increase in the distance between the

principal and the excited states rather than in a closer approach of their levels [2].

The authors do not believe that the changes in the absorption spectra of dyestuffs effected by hydrocarbon radicals that have been described in the present and previous reports are purely steric effects. There is no doubt that the steric effects may be reinforced by electronic influences. This is evident, for example, in preparations (IV) and (VIII) of the foregoing table. The phenyl group, despite its large bulk compared to that of the methyl group, causes a much smaller shift of the maximum. The electronic (auxochromic) action of saturated hydrocarbon radicals is not very great, however, and by itself it cannot produce the extremely large displacements of dyestuff absorption bands that we have observed.

## EXPERIMENTAL

The synthesis of the styryl dyestuffs (I), (II), (III), and (IV) have been described in the paper by Kipriyanov and Ushenko [3]. Dyestuff (V) has been described by Bloch and Hamer [4].

Ethyl perchlorate of 2-(p-dimethylamino-β-methylstyryl)-benzthiazole (VI). 0.5 g of 2-ethylbenzthiazole iodoethylate, 0.3 g of p-dimethylaminobenzaldehyde, and 2 ml of acetic anhydride were heated to the boiling point for 1 hour. 8 ml of ethyl alcohol and 0.5 g of sodium perchlorate dissolved in 5 ml of hot water were added to the solution. Crystals of the dye settled out when the mixture cooled. They were filtered out and washed with alcohol and with ether. The yield was 0.35 g, or 54% of the theoretical. The melting point was 234° with decomposition (the temperatures given herein are the corrected ones), after recrystallization from alcohol.

Found %: N 6.72.

$C_{20}H_{23}O_4N_2SCl$. Computed %: N 6.63.

Ethyl perchlorate of 2-(p-dimethylamino-β-ethylstyryl)-benzthiazole (VII).

The preparation was synthesized from 2-p-propylbenzthiazole iodoethylate by a method similar to that described above. We were unable to isolate it in the pure state.

Ethyl perchlorate of 2-(p-dimethyl-β-phenylstyryl)-benzthiazole (VIII). This was synthesized from 2-benzylbenzthiazole iodoethylate like the preceding compound. The yield was 18% of the theoretical. Minute cherry-red crystals; m.p. 172° with decomposition.

Found %: N 5.68.

$C_{25}H_{25}O_4N_2SCl$. Computed %: N 5.78.

Phenyl perchlorate of 2-(p-dimethylamino-α-methylstyryl)-benzthiazole (IX). This preparation was synthesized by the same method used for the preceding compound, from 0.9 g of 2-methylbenzthiazole bromophenylate and 0.5 g of p-dimethylaminoacetophenone in acetic anhydride. The precipitated dye perchlorate was dissolved in acetone, precipitated with water, filtered out, and recrystallized from alcohol. The yield was 0.26 g, or 29% of the theoretical; the m.p. was 215° with decomposition.

Found %: N 5.92.

$C_{24}H_{23}O_4N_2SCl$. Computed %: N 5.99.

Phenyl perchlorate of 2-(p-dimethylamino-α-phenylstyryl)-benzthiazole (X). 0.55 g of 2-methylbenzthiazole bromophenylate, 0.4 g of p-dimethylaminobenzophenone, and 3 ml of acetic anhydride were heated to boiling for 1.5 hours. 5 ml of alcohol and 5 ml of a hot 10% solution of sodium perchlorate were added to the solution. The precipitated dye was washed with acetone and ether. After recrystallization from alcohol the yield was 0.15 g, or 16% of the theoretical; the m.p. was 205° with decomposition.

Found %: N 5.16.
$C_{20}H_{23}O_4N_2SCl$. Computed %: N 5.23.

Ethyl perchlorate of 2-(p-dimethylamino-α-methylstyryl)-benzthiazole (XI). This preparation was synthesized from 1.2 g of 2-methylbenzthiazole ethyl-p-toluenesulfonate, 0.5 g of dimethylaminoacetophenone, and 3 ml of acetic anhydride by boiling them together for 1.5 hours. The dye was precipitated with sodium perchlorate and recrystallized from 30 ml of alcohol. The yield was 0.26 g or 34% of the theoretical. Large, lustrous red crystals; m.p. 203° with decomposition.

Found %: N 6.66; Cl 8.11.
$C_{20}H_{23}O_4N_2SCl$. Computed %: N 6.65; Cl 8.40.

## SUMMARY

A number of new styryl dyes have been synthesized by condensing the quaternary salts of 2-alkylbenzthiazoles with p-dimethylaminobenzaldehyde, p-dimethylaminoacetophenone, and p-dimethylaminobenzophenone. It has been shown that in all these preparations, which contain alkyl or aryl groups at the alpha or beta positions, the absorption maximum is shifted toward the shorter wavelengths, while the absorption intensity is sharply reduced. These phenomena have been connected with a disturbance of the coplanarity of the benzene and thiazole rings in the molecules of these dyes.

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* CB English translation, pp. 139 ff.

# THE SYNTHESIS OF NAPHTHACENE*

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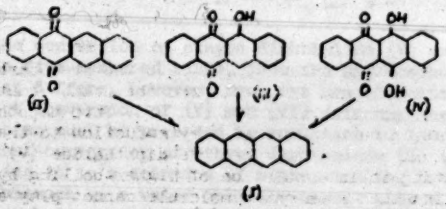
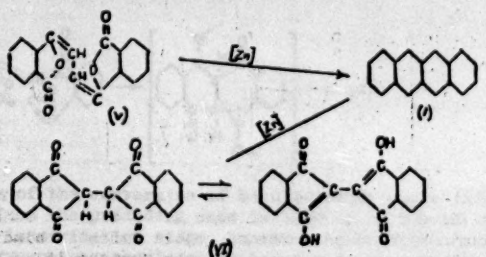
The golden-yellow hydrocarbon naphthacene (I) is synthesized by distilling naphthacenequinones and their hydroxy derivatives with zinc dust, i.e., from compounds that have the four-ring skeleton of naphthacene, such as compounds (II), (III), and (IV), [1,2]:

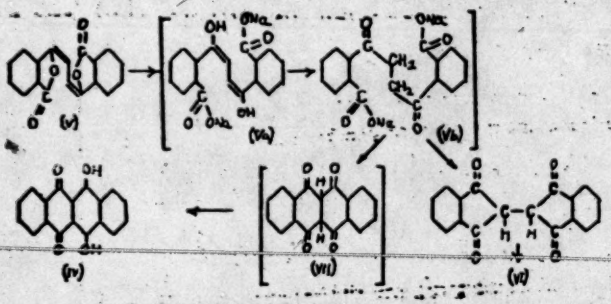


We found that naphthacene can be synthesized from compounds that do not possess this hydrocarbon's skeleton, viz., from such fairly accessible compounds as ethyne diphthalide (V) and bisdiketohydrindene (bisindandione) (VI) by distilling them with zinc dust in the presence of znhydrous zinc chloride.

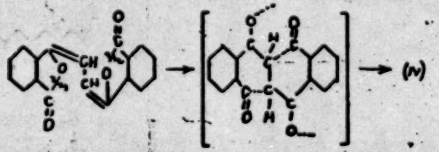


* Fourth report on the chemistry of naphthacene [3,4].

This interesting conversion reminds us of the isomerization of the light-yellow ethyne diphthalide (V) into the red dihydroxynaphthacenequinone (IV) and the bluish-violet bisdiketohydrindene (VI) by an alcoholic alkali, described in the literature [3]. In the first phase of this reaction we have to assume a hydrolytic opening of the anhydride rings [cf (Va) → (Vb)], followed by the detaching of water and the closing of the six-membered ring system (VII), which is more advantageous from the energy standpoint, and, in part, by the closing of the compound (VI):



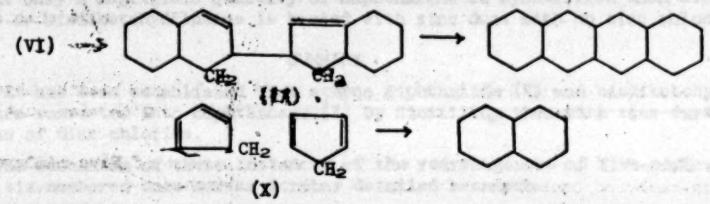
The mechanism of the conversion of ethyne diphthalide (V) and bisdiketohydrindene (VI), which contain five-membered rings, into the hydrocarbon naphthacene by distillation with zinc dust differs, however, from the transformation mechanism outlined above. In the direct conversion of (V) and (VI) into naphthacene described by us, the thermal isomerization must be preceded by reduction to the hydrocarbon. Thus, we have observed the gradual conversion of ethyne diphthalide (V) into dihydroxynaphthacenequinone (IV) by heating it in a solution of higher-boiling hydrocarbons (transformer-oil fraction). Inasmuch as a water molecule cannot play a part in this reaction, only thermal action being possible, we must assume that the conversion of ethyne diphthalide (V) to dihydroxynaphthacenequinone (IV) must begin with the ephemeral opening of the five-membered lactone rings, followed immediately by the closing of the stable system of dihydroxynaphthacenequinone (IV):



As for the mechanism of the conversion of bisdiketohydrindene (VI) into naphthacene, this differs from the preceding case in that we cannot be sure of the existence of a preliminary isomerization stage, inasmuch as bisdiketohydrindene is not converted into dihydroxynaphthacenequinone by heating it in a neutral high-

boiling solvent.

It is not impossible that in distillation with zinc dust the first phase of the reaction consists of the reduction of bisdiketohydrindene into the corresponding hydrocarbon (IX), after which the five-membered rings are isomerized, as in the well-known reaction involving the thermal condensation of cyclopentadiene (X) to naphthalene [5].




The instances of the synthesis of naphthacene described above are examples of the rearrangement of five-membered rings to more stable six-membered aromatic rings. It may be very interesting to continue the search for similar instances of this transformation, as well as to make a detailed study of the mechanism of these transformations.

## EXPERIMENTAL

1. Isomerization of ethyne diphthalide (V) to dihydroxynapthacenequinone (IV). 1 g of ethyne diphthalide was heated for 20 hours to 280-290° in 50 ml of the 200-220° (3 mm) fraction of refined transformer oil. As heating was continued, the ethyne diphthalide was isomerized to dihydroxynaphthacenequinone. As the solution cooled, yellow crystals of ethyne diphthalide settled out, together with the beautiful red needles of dihydroxynaphthacenequinone. Filtration yielded 0.6 g of crystals [a mixture of (V) and (IV)], which were recrystallized twice from nitrobenzene and then from tetrachloroethane.** This yielded 0.15 g (15%) of the dark-red crystals of dihydroxynaphthacenequinone, with a m.p. of 340° (determined in a Berl block).

2. Naphthacene from bisdiketohydrindene (VI). 1 g of bisdiketohydrindene was comminuted in a mortar with 2 g of zinc dust, 5 g of anhydrous zinc chloride, and 2 g of sodium chloride [6]. The mixture was placed in a 50-ml flask, whose neck was bent at a right angle, and gradually heated over a low burner flame. The reaction mass first turned black and then effervesced Fifteen minutes before effervescence ended the reaction mass was heated more strongly until the walls of the flask were dark red. This caused a brownish-yellow mixture of naphthacene and dihydronaphthacene to sublime; it condensed on the colder wall of the flask's neck. The sublimate was carefully mixed in a mortar with three times its weight of litharge, and the mixture was heated in a test tube to dehydrogenate the dihydronaphthacene. With rapid heating, the naphthacene sublimed as characteristic golden-orange leaflets (0.35 g). Recrystallization from boiling xylene yielded 0.25 g of pure naphthacene with a m.p. of 340 g. A test sample mixed with known naphthacene exhibited no depression. The naphthacene yield was about the same as the yield obtained by distilling dihydroxynaphthacenequinone (IV) or monohydroxynaphthacenequinone (III) [2] with zinc dust in

* Under different conditions, when heated in anhydrous pyridine, Vanag [4] succeeded in converting bisdiketohydrindene into dihydroxynaphthacenequinone. But Vanag was also unable to isomerize bisdiketohydrindene by merely heating it in an inert solvent (nitrobenzene).

** The tetrachloroethane solution must be filtered while hot, as the ethyne diphthalide also settles out if it is allowed to cool off completely. Separation may be effected by treating the mixture with 2N ammonia, in which only the bisdiketohydrindene dissolves.

the presence of zinc chloride.

3. Naphthacene from ethyne diphthalide (V). This reaction was carried out under exactly the same conditions as in the preceding experiment. 2 g of ethyne diphthalide yielded 0.22 g of pure naphthacene (11% of the theoretical). It is worthy of note that only a negligible quantity of naphthacene is synthesized when ethyne diphthalide or bisdiketohydrindene is heated with zinc dust with no zinc chloride present.

## SUMMARY

1. It has been established that ethyne diphthalide (V) and bisdiketohydrindene (VI) are converted into naphthacene (I) by distilling them with zinc dust in the presence of zinc chloride.

2. The mechanism of these instances of the rearrangement of five-membered rings into six-membered ones merits further detailed research.

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[5] Weger, Z. Ang. Chem., 22, 344 (1909).

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# THE STRUCTURE OF HALOGEN DERIVATIVES OF NAPHTHACENEQUINONE*

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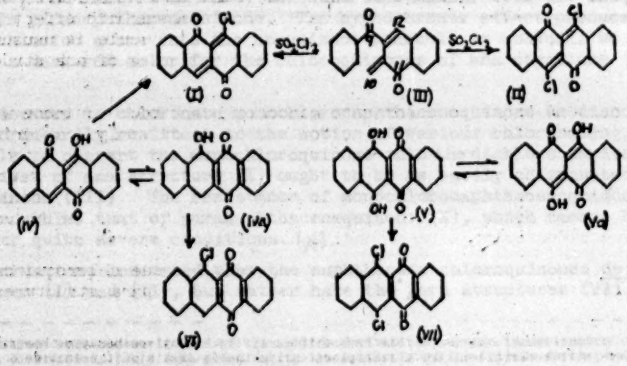
## I. MONOCHLORO AND DICHLORONAPHTHACENEQUINONES

Dichloronaphthacenequinone, first synthesized by Gabriel and Leupold [1] from dihydroxynaphthacenequinone (V) by reacting it with $PCl_5$ [1], was synthesized differently in 1940 by I. Postovsky and L. Goldyrev – by the action of $SO_2Cl_2$ upon the anaquinone (III) [2]. In this quinone the meso positions 10 and 12 are reactive, which is why the ana structure (II) resulted for the dichloronaphthacenequinone. Tautomerism, with the major role played by the ana form (Va), might be presupposed for dihydroxynaphthacenequinone (V), from which the identical dichloroquinone results.

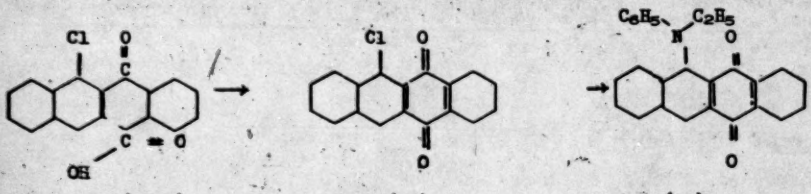
Inasmuch as not only dichloronaphthacenequinone, but the monochloronaphthacenequinone as well, could be synthesized from the ananaphthacenequinone (III), an ana structure (II) was also attributed to the monochloroquinone.




* Fifth report on the chemistry of naphthacene (tetracene).

But these conclusions regarding the ana structure of the mono- and dichlorides of naphthacenequinone (I, II), derived from what appeared to be the convincing reactions (III) ⟶ (I) and (III) ⟶ (II), contradicted the data of the previous authors [1], who ascribed a para structure (VI and VII) to the chlorides, besides being at variance with some of our own observations. It was difficult, for example, to reconcile the following facts with an ana sturcture for these compounds.

1) Monochloro-p-naphthacenequinone (VI) can be synthesized from 1-chloro-2-naphthoyl-o-benzoic acid (VIII), according to Waldmann [3]:




(VIII) (VI) (IX)

The only substance that can be formed in this reaction must have a para structure (VI). Any rearrangement to compound (VIII) during the process of ring closure is unlikely, and it therefore follows that the product (VI) must be different from the monochlorine derivative (I) prepared from the anaquinone (III). But when tested, both of these monochlorides were found to be identical in external appearance and melting point, and they caused no depression when mixed together in a test sample. We also proved the identity of these products by comparing the ethyl anilide derivatives (IX) synthesized from the monochlorine derivatives, from the anaquinone, and from the compound (VIII).*

2) Anaquinone (III) is reddish-orange. When chlorine atoms are introduced into its molecule, one should expect the color to grow deeper owing to the bathochromic effect of chlorine; but instead of that, the chlorides formed from the anaquinone are light yellow, like paranaphthacenequinone. The hypsochromic effect produced by the introduction of chlorine atoms into the anaquinone molecule is ususual: we should have expected a dark-red color for the chloroquinones of ana structure (I) and (II).

3) In our endeavors to chlorinate monochloronaphthacenequinone we discovered that it was extraordinarily resistant to the action of various chlorinating agents: we were unable to convert the monochloroquinone into the dichloro derivative. Monochlorine derivatives of ana structure (I) ought to be as easily chlorinated as the ananaphthacenequinone (III). The resistance of monochloronaphthacenequinone to chlorine, however, resembles that of paranaphthacenequinone (X), which cannot be chlorinated even under quite severe conditions. [2].

All these observations indicated that the naphthacene chloroquinones do not have the ana structures (I) and (II), but rather have the para structures (VI) and

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*. The ethyl anilide derivatives were chosen instead of the anilide derivatives because isomerization (cf below), which would interfere with observation, could take place during the synthesis of the anilide derivatives.

(VII), although they can be synthesized from the anaquinone. It followed that the reaction of ananaphthacenequinone (III) with sulfuryl chloride involves a peculiar rearrangement or reorganization of the central quinoid rings.

To clear up the problem of the structure of the chloronaphthacenequinones once for all, we resumed our work in this field in 1946, after several years of interruption. In view of the possibility of the foregoing rearrangement, we had to employ a method that excluded any farreaching chemical reaction in our investigation of the problem. We felt that polarographic investigation of these compounds would be especially suitable for this purpose, i.e., determining their halfwave potentials. We did this upon the assumption that the halfwave potentials ($E_{1/2}$) of compounds whose properties are as different as those of the para- and ananaphthacenequinones (X) and (III), will differ considerably, thus enabling us to assign the experimental values for the chloroquinones to one or another quinone of naphthacene. The table and Fig. 1 show the values of $E_{1/2}$ obtained for the substances in question, in volts with respect to a normal calomel electrode in 0.02N KCl as an electrolyte.

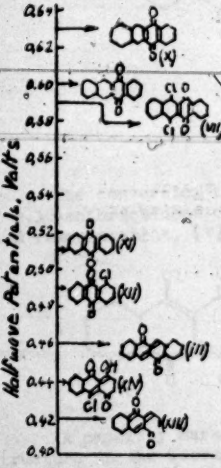



Fig. 1.

Halfwave Potentials of Quinones

| Name of substance | Halfwave potentials, volts | |
|---|---|---|
| | First halfwave | Second** halfwave |
| Anthraquinone (XI)..... | -0.51 | - |
| 1-Chloroanthraquinone (XII)..... | -0.49 | - |
| 1-Hydroxy-10-chloroanaquinone (XIV) *** | -0.44 | - |
| Ananaphthacenequinone (III)..... | -0.46 | -1.24 |
| Paranaphthacenaquinone (X)..... | -0.63 | -1.28 |
| Monochloronaphthacenequinone..... | -0.60 | -1.27 |
| Dichloronaphthacenequinone..... | -0.59 | -1.25 |

As the table and Fig. 1 indicate, the $E_{1/2}$ of paranaphthacenequinone and of the chloroquinones are more negative than the $E_{1/2}$ of ananaphthacenequinone.

It is known that chlorine atoms produce a shift of the $E_{1/2}$ toward positive values [5]. This is also seen when we compare the $E_{1/2}$ of 1-chloroanthraquinone (XII) with that of anthraquinone *** (XI) (cf Fig. 1 and the table).

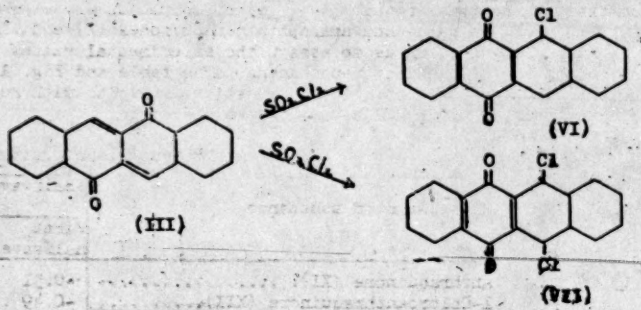
In Fig. 1 we see that the halfwave potentials for the chlorine derivatives of naphthacenequinone lie much higher than the halfwave potentials for the anaquinone and

* All the curves of naphthacenequinone derivatives exhibit a second wave (cf table). The values of $E_{1/2}$ for the second waves are nearly identical for the various derivatives, lying within the range of 1.25 - 1.30 volts. The presence of these waves may be due to the further reduction of the hydroquinones formed during the first stage. The synthesized hydroquinones and dihydro compounds have identical benzenoid location of the bonds for the para- and the anaquinones.

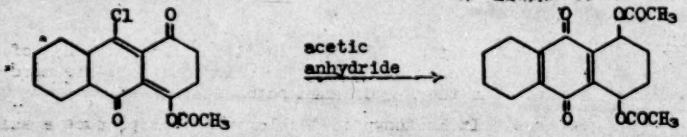
** Synthesized by the Green method [4].

*** The chlorine atom and the hydroxyl group exert opposite effects [5, e], which is why the shift of the $E_{1/2}$ for 1-hydroxy-10-chloroana-anthraquinone (XIV) is negligible, compared with that for the unsubstituted ana-anthraquinone (XIII). This quinone, which has not been synthesized as yet, ought to have an $E_{1/2}$ of about -0.42 to -0.43 volt, as

clearly approach the potential for paranaphthacenequinone rather than that for the anaquinone. If the chlorine derivatives of naphthacenequinone had the ana structures (I) and (II), their halfwave potentials would be somewhat more positive than that of the anaquinone, i.e., they would lie below that of anaquinone in the figure. It follows, therefore, that the chlorine derivatives of naphthacenequinone must be classed as belonging to the para series (VI and VII) and not to the ana series, as had been formerly supposed on the basis of the chlorination of ananaphthacenequinone [cf. (III) → (I) and (III) → (II)]. Hence, it must be assumed that the chlorination of ananaphthacenequinone by sulfuryl chloride involves a peculiar rearrangement, the mechanism of which is still unexplained.




The conversion of the derivatives of ana-anthraquinone into the derivatives of 9,10-anthraquinone described in the literature must be regarded as similar to this rearrangement, [7].




A paper by Marschalk and Stumm [8] appeared recently, entitled "Problems of Structure in the Tetracene Series," in which the para structure of the mono- and dichloronaphthacene quinones (VI and VII) was proved by chemical methods, i.e., these authors come to the same conclusions as we had reached chiefly from physico chemical measurements. Repeating the chlorination of ananaphthacenequinone with sulfuryl chloride described by us above, these authors, like us, observed the "anamolous" course of this reaction (the conversion of ananaphthacenequinone into derivatives of the paraquinone).

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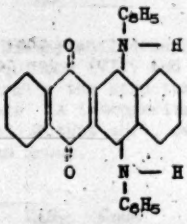
(cont. from previous page) against the 0.51 volt found for 9,10-anthraquinone (XI)

The results of the present research have been set forth by R. G. Beiles in his candidate's dissertation, submitted in February 1948 and defended in April 1948. The basic data contained in this dissertation are cited in the present report and in those to follow.

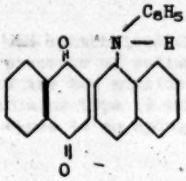
In connection with the publication of the paper by Marschalk and Stumm dealing with the same subject in which we are continuing our research, we must stress the fact that the problem of the structure of the chloroquinones of naphthacene raised by us has resulted in the discovery of an instance of the intramolecular reorganization of naphthacene quinones that is of theoretical interest, as well as in the discovery of 'ana reactions' in the chlorination of naphthacene (cf the following report).

## II. ANILIDE DERIVATIVES OF THE NAPHTHACENEQUINONES

Clearing up the structure of the naphthacene chloroquinones also defines more accurately the structure of the anilide derivatives produced by heating the chlorine or hydroxy derivatives of naphthacenequinone with aniline in the presence of sodium acetate. Paraquinone structures (XV) and (XVI) must be attributed to these anilide derivatives:



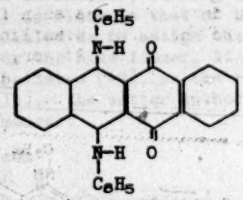
(XV)



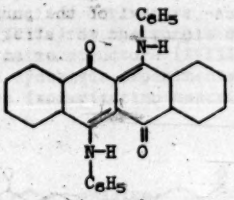
(XVI)

In a research project carried out with L.N.Goldyrev [2] we have shown that heating with aniline in the presence of boric acid results in the formation of isomeric anilide compounds, of which two isomers can be isolated in the pure state: a reddish-purple one with a m.p. of 244-246°, and a dark-blue one with a m.p. of 310-312°. These isomers proved to be quite stable in the pure state and did not undergo any change during eight years of storage.

At the beginning of our research on naphthacene we expressed the supposition that these anilide compounds are structural isomers – with para and ana structures: (XVIIa) and (XVIIb).



(XVII-a)



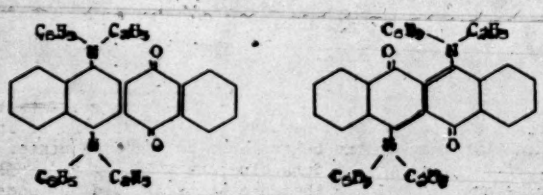
(XVIIb)

But, when we found that heating in a solution of aniline in the presence of boric acid results in the gradual isomerization of the anilides, i.e., that a mixture of the purple and blue isomers is formed for each of them, we concluded that these transformations are a special case of tautomerism [3].

In view of the fact that the initial chloroquinones had been proved to have a para structure, we were immediately able to illustrate this tautomerism by means of the formulas (XVIIa) ⇌ (XVIII):

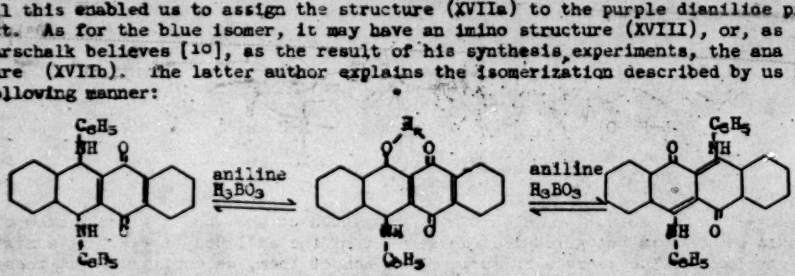
(XVIIa) (XVIII)

Diethylanilidonaphthacenequinone (XIX) was synthesized from dichloronaphthacenequinone (VII) and ethyl aniline in the presence of sodium acetate in order to determine the structural formulas of each of the two anilides, the blue and the purple. A tautomerism of the quinone-quinonimine type is impossible with a compound of this sort, owing to the fact that there is no hydrogen attached to the amino group.



(XIX) (XX)

Compound (XIX) consists of minute homogeneous reddish-purple crystals, which are soluble in benzene, turning it reddish-purple. The halfwave potential of compound (XIX) is close to that of the purple dianilide derivative, as seen in Fig. 2. All this enabled us to assign the structure (XVIIa) to the purple dianilide product. As for the blue isomer, it may have an imino structure (XVIII), or, as Marschalk believes [10], as the result of his synthesis experiments, the ana structure (XVIIb). The latter author explains the isomerization described by us in the following manner:




purple isomer (XXI) blue isomer

As confirmation of this scheme, Marschalk cites the formation of a monoanilide derivative (XXI) as a byproduct, noted by us previously [11].

To settle the problem of the structure of the blue isomer finally, it seems to us that an effort must be made to synthesise a diethylanilide compound with a known ana structure (XX, and to compare this compound with compound (XIX) and with the blue anilide isomer.

## EXPERIMENTAL

1. Polarographic investigation of polycyclic quinones. This polarographic investigation was made with the visual polarograph designed by A. G. Stromberg (of the Urals branch of the USSR Academy of Sciences). The anode was a normal calomel half-cell; while the cathode was a mercury drop electrode, immersed in the tested solution. The cathode and anode were connected through an agar-agar switch filled with a saturated solution of KCl.

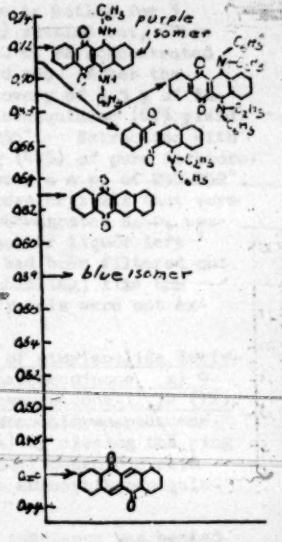



Fig. 2

In selecting a solvent for the naphthacene derivatives we met with difficulties due to the low solubility of these compounds. After a series of tests, we decided upon the following method: a weighed quantity of the quinone, based on a concentration of $1 \cdot 10^{-3}$ mol, was dissolved, with heating, in 0.2 ml of cryoscopically pure benzene, and then 2.2 ml of alcohol and 0.6 ml of 0.1N KCl plus 2 drops of a 0.5% solution of gelatin were added. Solutions prepared in this manner may be used satisfactorily, although a precipitate sometimes settles out when hydrogen is passed through for a long time prior to the beginning of measurement. It is then advisable to substitute isopropyl alcohol for the ethyl alcohol.

Owing to the low solubility of naphthacene derivatives, we had to dispense with the employment of buffer mixtures, for this would have caused the quinones to settle out as precipitates, due to the higher salt concentration.

A current of purified hydrogen was passed through the solution for 10-15 minutes prior to each run. After the curve had been plotted, hydrogen was passed through for another 10 minutes, and the curve was plotted once more, after which the whole operation was repeated. The discrepancies between the values of $E_{1/2}$ found in parallel runs did not exceed 0.02 volt; the temperature of the runs was 19°.

By way of example, we reproduce the polarograms for anaanphthacenequinone, paranaphthacenequinone, and monochloronaphthacenequinone (for the first halfwave) in Fig. 3.

2. Synthesis of 9,10-dichloronaphthacenequinone-11,12 (/II/). Dichloronaphthacenequinone is synthesized, according to Gabriel [4], by reacting $PCl_5$ with

dihydroxynaphthacenequinone in boiling nitrobenzene (20% yield) or with a good yield by the method described by us previously [2]. The following method is better. 20 g of $PCl_5$ is added in several batches to 6 g of dihydroxynaphthacenequinone dissolved, with heating, in 100 ml of tetrachloroethane, and the reaction mixture is boiled for 3 hours. After cooling, light-yellow lamellae (a "complex", 5.2 g) settled out; after filtering and drying they were heated to 60-70° for 1 hour in 100 ml of concentrated $H_2SO_4$. This caused the evolution of HCl, and the solution turned red. After the solution had cooled, pouring it out over ice resulted in the recovery of 4.5 g of impure dichloronaphthacenequinone (67% yield) with a m.p. of 230-235°. Extraction with xylene yielded 3.0 g (44%) of pure dichloronaphthacenequinone with a m.p. of 250-252°. Some 0.6 g of colorless crystals that were not decomposed by concentrated $H_2SO_4$ was recovered from the mother liquor left after the "complex" had been filtered out by evaporation and chilling; like the "complex," these crystals were not examined any further.

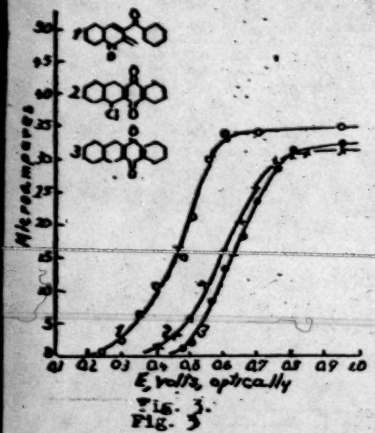


Fig. 3.

3. Synthesis of ethylanilide derivatives of peranaphthacenequinone. a) 9-Ethylanilidonaphthacenequinone-11,12 (IX). We used samples of monochloronapthacenequinone prepared: 1) by closing the ring of 1-chloro-2-naphthoyl-o-benzoic acid (VIII); and 2) from ananaphthacenequinone and $SO_2Cl_2$.

0.2 g of the substance was heated with 2 ml of freshly distilled ethylaniline to 180-190° for 3 hours in the presence of 0.2 g of dehydrated sodium acetate. Toward the end of the reaction the solution turned dark red. After it had cooled and had been diluted with 5 volumes of alcohol, crystals settled out within a few hours; they were filtered out, washed with alcohol, and recrystallized from glacial acetic acid.

This resulted in the recovery of 0.2-0.22 g of beautiful gleaming reddish-purple lamellae with a m.p. of 208-210°; under the microscope they were transparent orange rectangles. A mixed test sample of samples 1 and 2 exhibited no depression of the melting point.

1) 3.215 mg substance: 0.118 ml $N_2$ (21°, 732 mm).
4.900 mg substance: 0.176 ml $N_2$ (20°, 731 mm).
Found %: N 4.01, 3.95.
$C_{28}H_{19}O_2N$. Computed %: N 3.71.

2) 6.120 ml substance: 0.196 ml $N_2$ (19°, 740 mm).
5.840 ml substance: 0.186 ml $N_2$ (18°, 740 mm).
Found %: N 3.67, 3.64.
$C_{28}H_{19}O_2N$. Computed %: N 3.71.

b) 9,10-Diethylanilidonaphthacenequinone-11,12 (XIX). This substance was synthesized from dichloronaphthacenequinone by the method given for the monoethyl anilide derivative. It is a reddish-purple crystalline powder with a m.p. of 222-224°; under the microscope it consists of minute orange-red lamellae with broken edges.

3.360 mg substance: 0.157 ml $N_2$ (18°, 735 mm).
5.530 mg substance: 0.269 ml $N_2$ (19°, 735 mm).
Found %: N 5.42, 5.58.
$C_{34}H_{28}O_2N_2$. Computed %: N 5.65.

## SUMMARY

1. The chlorination of the anaquinone (III) by sulfuryl chloride, cited in our previous paper [2], indicates that the chloronaphthacenequinones (I) and (II) have ana structures; on the other hand, several facts bear witness to the para structure of these compounds – (VI) and (VII).

2. The results of polarographic investigation – determining the halfwave potentials of these compounds – confirmed their paraquinoid structure (VI and VII). Hence, the purple dianilide derivative likewise has a para structure (XV).

3. These data indicate that an intramolecular reorganization of anaphthacenequinone (III) takes place during its reaction with sulfuryl chloride, as a result of which chlorine derivatives of paranaphthacenequinone – (VI and VII) – are formed instead of the expected ana derivatives (I and II).

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# THE DERIVATIVES OF ACETYLENE

## 107. SYNTHESIS OF POLYCYCLIC COMPOUNDS RELATED TO THE STEROIDS

## IV. THE DIENE CONDENSATION OF 1,3-DIMETHYL-$\Delta^1$-CYCLOPENTEN-5-ONE AND 1,3-DIMETHYL-$\Delta^1$-CYCLOPENTENE-4,5-DIONE WITH α- AND β-VINYLOCTAHYDRONAPHTHALENES

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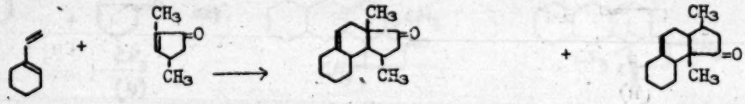
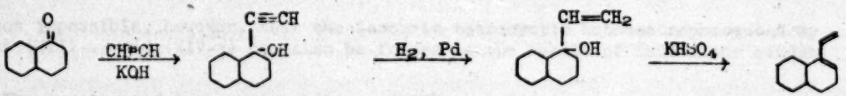
In our previous research [1] we discovered that 1,3-dimethyl-$\Delta'$-cyclopenten-5-one (II) enters fairly readily into a diene synthesis with 1-vinyl-$\Delta'$-cyclohexene (I), forming the tricyclic ketones (III) and (IV) with angular methyl groups:

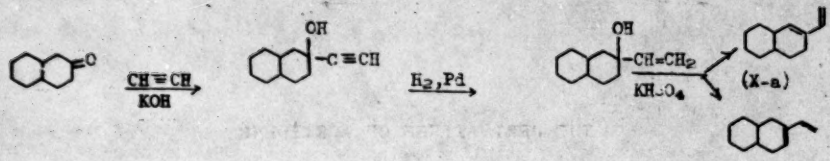


(I) (II) (III) (IV)

This simple method of synthesizing polycyclic ketones containing a cyclopentanone ring and an angular methyl group may be employed to synthesize steroid compounds, which play such an important role in the activity of the animal organism. By way of a model approach to the synthesis of steroid compounds, we undertook a study of the ability of 1,3-dimethyl-$\Delta'$-cyclopenten-5-one (II) to enter into diene synthesis with α- and β-vinyloctahydronaphthalenes. We synthesized these dienes as follows:

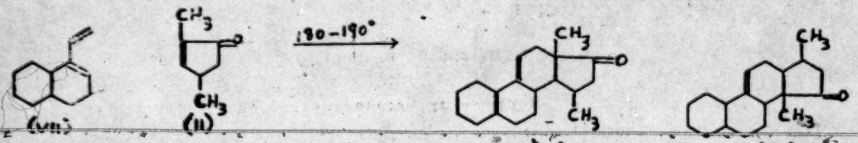


(V) (VI) (VII)



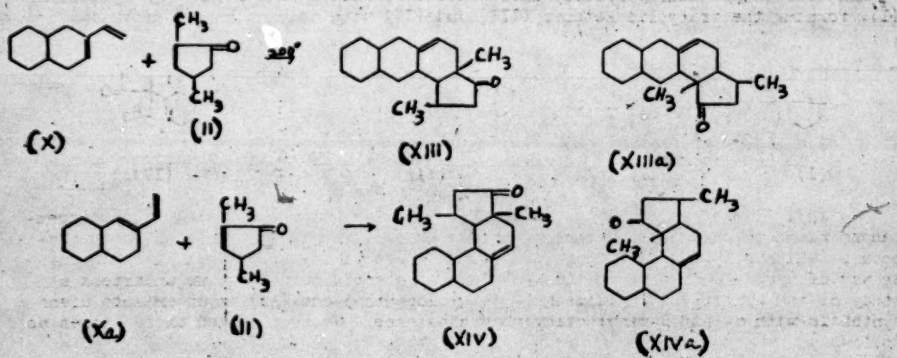

(VIII) (IX) (X)

When 1,3-dimethyl-$\Delta^1$-cyclopenten-5-one (II) is heated to 180-190° for 7 hours with trans-α-vinyloctahydronaphthalene (VII), we get a yield of approximately 50% of a mixture of crystalline tetracyclic ketones (XI) and (XII), with the composition of $C_{15}H_{28}O$:




(VII) (II) (XI) (XII)

When 1,3-dimethyl-$\Delta^1$-cyclopenten-5-one (II) is heated to 198-200° for 6 hours with the cis-β-vinyloctahydronaphthalenes (X) and (X-a), two liquid isomeric tetracyclic ketones with the composition of $C_{15}H_{28}O$, whose structure is given by Formulas (XIII) and (XIV), are formed:

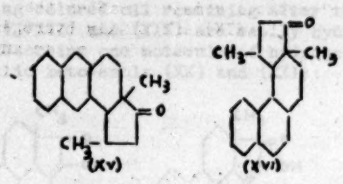



(X) (II) (XIII) (XIIIa)

(Xa) (II) (XIV) (XIVa)

It is not impossible, however, that the isomeric tetracyclic ketones represented by Formulas (XIII-a) and (XIV-a) can also be formed as the result of this diene condensation.

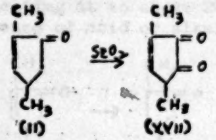
The unsaturated tetracyclic ketones (XIII) and (XIV) are readily hydrogenated over a Pt catalyst in anhydrous acetic acid, adding one molecule of hydrogen and forming the corresponding saturated tetracyclic ketones (XV) and (XVI):



(XV) (XVI)

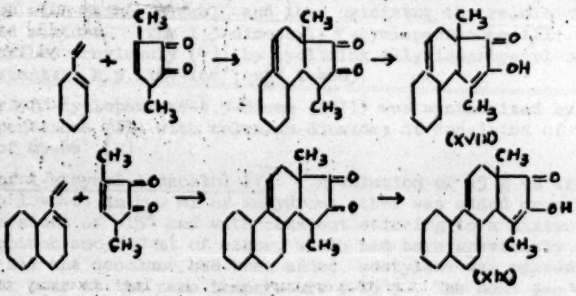
It has thus been established that 1,3-dimethyl-Δ'-cyclopenteh-5-one (II) can enter into diene synthesis with α- and β- vinyloctahydronaphthalenes, giving rise to tetracyclic cyclopentanophenanthrene ketones with an angular methyl group.

1,3-Dimethyl-Δ'-cyclopentene-4,5-dione (XVII) has been recently synthesized in our laboratory by oxidizing 1,3-dimethyl-Δ'-cyclopenten-5-one (II) with selenium dioxide:



(II) (XVII)

Inasmuch as the dione (XVII) is more reactive in diene syntheses than the 1,3-dimethyl-Δ'-cyclopenten-5-one (II), because it has two carbonyl groups, we were interested in exploring the condensation of this dione with 1-vinyl-Δ'-cyclohexere, as well as with the α- and β-vinyloctahydronaphthalenes. We found that the dione (XVII) actually enters in diene synthesis with 1-vinyl-Δ'-cyclohexene and α-vinyloctahydronaphthalene readily, giving rise to the colorless crystalline keto-enols (XVIII) and (XIX):



(XVIII)

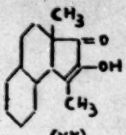
(XIX)

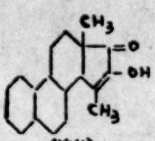
This sort of enolization of polycyclic α-diketones has been studied in detail in our laboratory, using other substances as examples [2].

We were unable to isolate cyrstalline products after condensing the dione (XVII) with the β-vinyloctahydronaphthalenes (X) and (X-a), recovering a very viscous substance that was hard to identify.

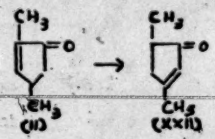
The keto-enol (XVIII) turns yellow upon standing in an alcoholic or acetic-acid

solution, a non-crystallizing colored oil remaining after the solvent is driven off. The unsaturated keto-enols (XVIII) and (XIX) are easily hydrogenated over a Pt catalyst in anhydrous acetic acid, absorbing one molecule of hydrogen and giving rise to the corresponding saturated cyclic keto-enols (XX) and (XXI):


(XX)


(XXI)

It has been recently shown in our laboratory that 1,3-dimethyl-$\Delta^4$-cyclopenten--5-one (II) is isomerized to 1,3-dimethyl-$\Delta^3$-cyclopenten-5-one (XXII), with the double bond shifted along the ring, by heating it to above 200° for a long time, or, even better, by heating it in the presence of acid or alkaline catalysts:


(II) (XXII)

As might have been expected, the cyclopentenone (XXII) enters into diene synthesis with great difficulty, no products of diene condensation being recovered after it had been heated for 20 hours to temperatures of 130 and 200° with 1-vinyl-$\Delta^3$-cyclohexene.

## EXPERIMENTAL

The initial α- and β-decalones were prepared by hydrogenating α- and β-naphthols in an autoclave with Rainey nickel, and then oxidizing the resulting decalols with a chromic acid mixture. The 1,3-dimethyl-$\Delta^4$-cyclopentenone (II) was synthesized by the method described previously [3]: by cyclizing allylisopropenyl ketone; it had the following constants: b.p. 164-166°; $n_D^{20}$ 1.4665.

1,3-Dimethyl-$\Delta^4$-cyclopentene-4,5-dione (XVII) was synthesized by oxidizing the dimethylcyclopentenone (II) with selenium dioxide; it consisted of yellow crystals with a m.p. of 65-66° [2].

Synthesis of 1-ethynyl-1-decalol (V). A solution of 45 g of trans-α-decalone (m.p. 31-33°, $n_D^{21}$ 1.4840) in 200 ml of anhydrous ether was added drop by drop during 3 hours at a temperature of -15° and with constant stirring to a mixture of 21 g of powdered caustic potash and 500 ml of ether, which had been previously saturated with acetylene. After all the decolone had been added, acetylene was passed through the mixture for another hour at the same temperature (-15°). The next day the mixture was treated with water, and the ether layer was separated, washed with 5% hydrochloric acid and then with water, and desiccated over sodium sulfate. Fractionation of the reaction product in vacuum yielded 37 g of 1-ethynyl-1-decalol (V), b.p. 105-107° at 5 mm:

$n_D^{20}$ 1.5030; $d_4^{20}$ 1.0098; $MR_D$ found 52.47; computed 52.73.

4.240 mg substance: 12.490 mg $CO_2$; 3.885 mg $H_2O$.

5.620 mg substance: 16.55 mg $CO_2$; 5.095 mg $H_2O$.

Found %: C 80.39, 80.20; H 10.25, 10.14.

$C_{12}H_{18}O$. Computed %: C 80.89; H 10.18.

Synthesis of 1-vinyl-1-decalol (VI). 30 g of the acetylene alcohol (V) was hydrogenated in 50 ml of ethyl alcohol over a Pd catalyst. 3.8 liters of hydrogen (1 mol) were absorbed during eight hours. This yielded 28.5 g of 1-vinyl-1-decalol (VI) b.p. 118-119° at 12 mm:

$n_D^{20}$ 1.5040; $d_4^{20}$ 0.9915; $MR_D$ found 53.74; computed 54.26.
5.225 mg substance: 15.274 mg $CO_2$; 5.298 mg $H_2O$.
Found %: C 79.74; H 11.34.
$C_{12}H_{20}O$. Computed %: C 80.00; H 11.11.

Dehydration of 1-vinyl-1-decalol (VI). A mixture of 28 g of 1-vinyl-1-decalol (VI) and 14 g of anhydrous, finely powdered potassium bisulfate was heated in a current of nitrogen and at a vacuum of 34 mm and a bath temperature of 150-160°. This drove water and a hydrocarbon off. The product was extracted with ether, desiccated with calcium chloride, and fractionated in vacuum. This yielded 15 g of 1-vinyl-Δ'-octalin (VII), as a colorless liquid with a b.p. of 104-105° at 13 mm.

$n_D^{20}$ 1.5170; $d_4^{20}$ 0.9366; $MR_D$ found 52.38; computed 52.28.
4.596 mg substance: 14.884 mg $CO_2$; 4.594 mg $H_2O$.
Found %: C 88.5; H 11.2.
$C_{12}H_{18}$. Computed %: C 88.9; H 11.1.

Condensation of 1-vinyl-Δ'-octalin (VII) with maleic anhydride yielded the anhydride of Δ⁴-dodecahydrophenanthrene-1,2-dicarboxylic acid, which fused at 139°.

4.760 mg substance: 12.845 mg $CO_2$; 3.285 mg $H_2O$.
5.420 mg substance: 14.088 mg $CO_2$; 3.555 mg $H_2O$.
Found %: C 73.64, 73.65; H 7.72, 7.62.
$C_{16}H_{20}O_3$. Computed %: C 73.84; H 7.69.

Condensation of 1-vinyl-Δ'-octalin with 1,3-dimethyl-Δ'-cyclopenten-5-one. A mixture of 7 g of the diene (VII) and 21 g of the dimethylcyclopentenone (II) was heated to 180-190° for 7 hours. Fractionation of the reaction products yielded 25 g of the initial substances and 4 g of condensation products with a b.p. of 170-178° at 3 mm; $n_D^{20}$ 1.5320. Dilution of the condensation products with ether and chilling yielded 2 g of a mixture of the crystalline ketones (XI) and (XII) with a m.p. of 72-88°:

3.520 mg substance: 10.798 mg $CO_2$; 3.200 mg $H_2O$.
4.760 mg substance: 14.589 mg $CO_2$; 4.418 mg $H_2O$.
Found %: C 83.73, 83.70; H 10.17, 10.38.
$C_{18}H_{28}O$. Computed %: C 83.82; H 10.29.

Repeated recrystallization of these crystals from methanol yielded the individual tetracyclic ketone (XI) or (XII) with a m.p. of 132-133°:

4.375 mg substance: 13.400 mg $CO_2$; 4.015 mg $H_2O$.
4.160 mg substance: 12.778 mg $CO_2$; 3.840 mg $H_2O$.
Found %: C 83.58, 83.82; H 10.26, 10.33.
$C_{18}H_{28}O$. Computed %: C 83.82; H 10.29.

The synthesized ketone does not form a semicarbazone, even when heated. Distillation of the mother liquor, after the crystalline ketone with a m.p. of 72-88° had been filtered out, yielded about 1 g of a substance with a b.p. of 179-182° at 4 mm; $n_D^{27}$ 1.5230, which also crystallizes after standing for one month. Recrystallization of this product from methanol yielded 0.5 g of the individual tetracyclic ketone (XI) or (XII), with a m.p. of 70-72°.

4.200 mg substance: 12.920 mg $CO_2$; 3.955 mg $H_2O$.
4.475 mg substance: 13.740 mg $CO_2$; 4.160 mg $H_2O$.
Found %: C 83.95, 83.79; H 10.54, 10.40.
$C_{18}H_{28}O$. Computed %: C 83.82; H 10.29.

The 2,4-dinitrophenylhydrazone of this ketone melted at 208-210° (from ethyl alcohol):

4.160 mg substance: 0.505 ml $N_2$ (22°, 731 mm).
2.690 mg substance: 0.324 ml $N_2$ (21°, 731 mm).
Found %: N 13.9, 13.9.
$C_{25}H_{32}O_4N_4$. Computed %: N 12.4.

Synthesis of 2-ethynyl-2-decalol (VIII). The 2-ethynyl-2-decalol (VIII) described in the literature [4] was synthesized with a yield of 70% by condensing the β-decalol (b.p. 116-118° at 15 mm; $n_D^{20}$ 1.4880) with acetylene in the presence of caustic potash as described above. The alcohol thus synthesized was a thick colorless liquid with a b.p. of 115-118° at 8 mm; $n_D^{20}$ 1.5060.

Synthesis of 2-vinyl-2-decalol (IX). 25 g of 2-ethynyl-2-decalol (VIII) was hydrogenated with a Pd catalyst in a solution of 40 ml of methanol. 3.3 liters of hydrogen (1 mol) were added during 6.5 hours, after which hydrogenation was broken off. Fraction of the hydrogenation product yielded 24 g of 2-vinyl-2-decalol (IX) as colorless liquid with a b.p. of 119-120° at 7 mm:

$n_D^{20}$ 1.5050; $d_4^{20}$ 0.9965; $MR_D$ found 53.50; computed 54.27.
11.91 mg substance: 34.84 mg $CO_2$; 12.30 mg $H_2O$.
10.99 mg substance: 32.23 mg $CO_2$; 11.57 mg $H_2O$.
Found %: C 79.83, 80.03; H 11.55, 11.78.
$C_{12}H_{20}O$. Computed %: C 80.00; H 11.11.

Dehydration of 2-vinyl-2-decalol (IX). A mixture of 15 g of 2-vinyl-2-decalol (IX) and 6 g of finely powdered potassium bisulfate was heated for 20 minutes to 150-160° in a current of nitrogen. Then the reaction products were driven off completely in vacuum, desiccated with calcium chloride, and redistilled in vacuum. This yielded 7 g of the β-vinyloctalins (X) and (X-a) as a colorless liquid with a b.p. of 132-134° at 50 mm;

$n_D^{20}$ 1.5180; $d_4^{20}$ 0.9274; $MR_D$ found 52.75; computed 52.28.
4.650 mg substance: 15.010 mg $CO_2$; 4.670 mg $H_2O$.
Found %: C 88.4; H 11.2.
$C_{12}H_{18}$. Computed %: C 88.88; H 11.12.

Condensation of beta vinyloctalins with maleic anhydride yielded a crystalline addition product that fused at 115-117° (with decomp.);

10.52 mg substance: 28.37 mg $CO_2$; 7.52 mg $H_2O$.
7.62 mg substance: 20.59 mg $CO_2$; 5.52 mg $H_2O$.
Found %: C 73.59, 73.74; H 8.02, 8.04.
$C_{16}H_{20}O_3$. Computed %: C 73.84; H 7.69.

The synthesized product is most probably a mixture of the anhydrides of $\Delta^3$-dodecahydroanthracene-1,2-dicarboxylic acid and $\Delta^4$-dodecahydroanthracene-5,6-dicarboxylic acid.

Condensation of β-vinyloctalins (X) and (X-a) with 1,3-dimethyl-$\Delta^4$-cyclopenten-5-one. A mixture of 14 g of the β-vinyloctalins (X) and (X-a), 25 g of 1,3-dimethyl-$\Delta^4$-cyclopenten-5-one (II), and 0.4 g of pyrogallol was heated for 6 hours to 198-200° in a metallic ampoule. Fractionation of the reaction products in vacuum yielded the

following fractions:

1) b.p. 68-84° at 24 mm: 27 g
2) b.p. 158-162° at 1 mm: 7 g
3) b.p. 172-178° at 1 mm: 3 g.

The first fraction is a mixture of the initial substances – the beta vinyloctalins (X) and (X-a) and the dimethylcyclopentenone (II). Refractionation of fraction 2 yielded 4 g of the tetracyclic ketone (XIII) or (XIV) with a b.p. of 155-156° at 2 mm:

$n_D^{20}$ 1.5290; $d_4^{20}$ 1.0398; $MR_D$ found 80.66; computed 80.68.
5.372 mg substance: 16.417 mg $CO_2$; 4.942 mg $H_2O$.
5.028 mg substance: 15.374 mg $CO_2$; 4.620 mg $H_2O$.
Found %: C 83.40, 83.44; H 10.30, 10.28.
$C_{18}H_{28}O$. Computed %: C 83.82; H 10.28.

2.5 g of this ketone was hydrogenated with a Pt catalyst in a solution of 20 ml of alcohol. 200 ml of hydrogen (1 mol) was absorbed in 4 hours, yielding 2.2 g of the saturated tetracyclic ketone (XV or XVI), with a b.p. of 156-158° at 2 mm; $n_D^{20}$ 1.5220.

5.148 mg substance: 15.653 mg $CO_2$; 4.880 mg $H_2O$.
Found %: C 82.8; H 10.6.
$C_{18}H_{30}O$. Computed %: C 83.2; H 10.9.

Refractionation of Fraction 3 yielded 2 g of the tetracyclic ketone (XIII or XIV), as a viscous, colorless liquid with a b.p. of 179-181° at 3 mm; $n_D^{20}$ 1.5320:

6.400 mg substance: 19.722 mg $CO_2$; 5.985 mg $H_2O$.
4.130 mg substance: 12.707 mg $CO_2$; 3.767 mg $H_2O$.
Found %: C 84.10, 83.97; H 10.47, 10.21.
$C_{18}H_{28}O$. Computed %: C 83.82; H 10.29.

3.5 g of this ketone was hydrogenated with a Pt catalyst in a solution of 30 ml of ethyl alcohol. 100 ml of hydrogen was added during 1.5 hours, and hydrogenation was stopped. After the alcohol had been driven off and some more catalyst had been added, the product was rehydrogenated in a solution of 20 ml of anhydrous acetic acid. Another 200 ml of hydrogen was absorbed during 45 minutes. This yielded 3 g of a saturated tetracyclic ketone (XV or XVI) with a b.p. of 169-174° at 3 mm; $n_D^{20}$ 1.5200.

7.185 mg substance: 21.890 mg $CO_2$; 7.007 mg $H_2O$.
4.805 mg substance: 14.649 mg $CO_2$; 4.707 mg $H_2O$.
Found %: C 83.14, 83.20; H 10.91, 10.98.
$C_{18}H_{30}O$. Computed %: C 83.21; H 10.94.

We were unable to isolate the pure crystalline derivatives of the foregoing tetracyclic ketones. The semicarbazones and oximes were usually recovered as oils, while the 2,4-nitrophenylhydrazones yielded 1.5-2% more nitrogen upon analysis than called for by theory.

Condensation of 1-vinyl-$\Delta^1$-cyclohexene with 1,3-dimethyl-$\Delta^1$-cyclopentene-4,5-dione. A mixture of 5 g of 1-vinyl-$\Delta^1$-cyclohexene (I) (b.p. 143-145°; $n_D^{18}$ 1.4900), 2.5 g of the dione (XVII), and 15 g of dioxane was heated for 20 hours to 130°. This yielded 3 g of colorless crystals of the ketenol (XVIII), which fused at 111-112° after double recrystallization from methanol:

5.960 mg substance: 16.912 mg $CO_2$; 4.600 mg $H_2O$.
4.550 mg substance: 14.010 mg $CO_2$; 3.827 mg $H_2O$.
Found %: C 77.43, 77.24; H 8.63, 8.65.
$C_{15}H_{20}O_2$. Computed %: C 77.58; H 8.61.

0.15 g substance: 10 ml $CH_4$ (26°, 740 mm).
Found %: OH 4.59.
$C_{15}H_{18}O(OH)$. Computed %: OH 7.32.

A solution (alcoholic or acetic-acid) of the keto-enol (XVIII) turns yellow upon standing, and a yellow noncrystallizing oil is left after the solvent is driven off. The substance is not hydrogenated over a Pd catalyst in ether. One molecule of hydrogen is added during hydrogenation with a Pt catalyst in anhydrous acetic acid. Eliminating the solvent yielded yellow crystals of the keto-enol (XVIII) with a m.p. of 113-118°, which fused at 120-124° after double recrystallization from methanol:

5.405 mg substance: 15.132 mg $CO_2$; 4.125 mg $H_2O$.
4.320 mg substance: 12.075 mg $CO_2$; 3.335 mg $H_2O$.
Found %: C 76.35, 76.28; H 8.54, 8.64.
$C_{15}H_{22}O_2$. Computed %: C 76.92; H 9.40.

Condensation of 1-vinyl-$\Delta^1$-octalin with 1,3-dimethyl-$\Delta^1$-cyclopentene-4,5-dione. A mixture of 2 g of the dione (XVII), 3 g of 1-vinyl-$\Delta^1$-octalin (VII), and 20 g of dioxane was heated for 5 hours to 128-130°. Elimination of the solvent yielded 4.7 g of viscous products, the chilling of which yielded 1 g of colorless crystals of a tetracyclic keto-enol (XIX) with a m.p. of 199-201° (from ethyl alcohol):

5.160 mg substance: 15.022 mg $CO_2$; 4.215 mg $H_2O$.
11.270 mg substance: 32.910 mg $CO_2$; 9.200 mg $H_2O$.
Found %: C 79.45, 79.69; H 9.14, 9.13.
$C_{19}H_{26}O_2$. Computed %: C 79.92; H 9.09.
0.12 g substance: 8 ml $CH_4$ (26°, 740 mm).
Found %: OH 4.49.
$C_{19}H_{25}O(OH)$. Computed %: OH 5.96.

0.8 g of the unsaturated keto-enol (XIX) described above was hydrogenated with a Pt catalyst in 50 ml of anhydrous acetic acid. 120 ml of hydrogen was added in 35 minutes. A mixture of colorless crystalline products that fused at 141-145° was recovered. Repeated recrystallization from ethyl alcohol yielded 0.3 g of crystals of a tetracyclic keto-enol (XXI) with a m.p. of 140-142°:

3.597 mg substance: 10.475 mg $CO_2$; 3.183 mg $H_2O$.
3.165 mg substance: 9.210 mg $CO_2$; 2.831 mg $H_2O$.
Found %: C 79.47, 79.41; H 9.90, 10.01.
$C_{19}H_{28}O_2$. Computed %: C 79.61; H 9.73.

## SUMMARY

Condensation of 1,3-dimethyl-$\Delta^1$-cyclopenten-5-one (II) with α-vinyloctalin (VII) and β-vinyloctalin (X) results in an approximately 50% yield of the tetracyclic ketones (XI) and (XIII), which contain the cyclopentanone ring with an angular methyl group that is typical of steroid compounds. Condensation of the vinylcyclohexene (I) and the α-vinyloctalin (VII) with 1,3-dimethyl-$\Delta^1$-cyclopentene-4,5-dione (XVII) yields the corresponding tetracyclic diones, which exist in their enolic forms (XVIII) and (XIX). A description is given of the hydrogenated derivatives of the synthesized cyclic compounds.

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*See CB translation p. 2211 ff.

# RESEARCHES ON THE HYDROXYFUCHSONE DYES

## XII. ACID TRANSFORMATIONS OF METHOXYFUCHSONE DERIVATIVES [1]

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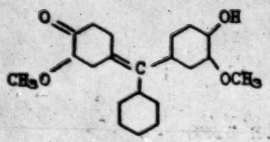
In the synthesis of 3,3'-dimethoxybenzaurin (I) [2] we noticed that the crystals of the hydrochloride of the dye, which settle out as a precipitate when a solution of a bisulfite derivative is decomposed with hydrochloric acid, gradually resinify when heating of the suspension is continued and are converted into some new substance; the latter differs from the dye in that it does not form colored acid salts and does not react with bisulfite, but is soluble in alkali, though without the blue color that is characteristic of the dye. This product of the acid transformations of 3,3'-dimethoxybenzaurin is recovered as dark, tarry curds, which upon cooling harden into a brownish-yellow mass that can be ground to a yellow powder. It has been found that the 3,3'-dimethoxybenzaurin previously isolated likewise undergoes such transformations when heated with hydrochloric or sulfuric acid.

We subsequently discovered that 3,3',3''-trimethoxyaurin (II) undergoes similar transformations; heating the hydrochloride of this dye (rubrocol) with mineral acids also converts it into a new resinous substance, which is no longer acid-soluble and does not form bisulfite derivatives.

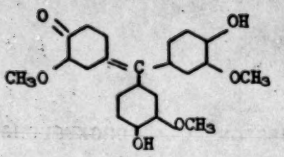
For the sake of comparison, we also subjected hydroxyfuchsone dyes that contained no methoxy groups - benzaurin and aurin - to heating with mineral acids. We found that when aurin is boiled even with 15% hydrochloric acid, it undergoes no change whatsoever during 30 days: the resulting suspension of the hydrochloride of the dye is fully soluble in aqueous bisulfite, and treating it with sodium acetate yields aurin with a melting point that agrees with that of the pure dye.

Benzaurin likewise proved resistant to boiling with acids. Nonetheless, it differed from aurin in that it was no longer completely soluble in bisulfite after several days of boiling with concentrated hydrochloric acid; we isolated a pure substance identified as 4-hydroxydiphenyl ketone [1] from the insignificant quantity of precipitate.

This comparison indicates that it is the presence of methoxy groups in 3,3'-dimethoxybenzaurin (I) and 3,3',3''-trimethoxyaurin (II) that is responsible for the specific transformations of these hydroxyfuchsone dyes when they are boiled with acids. We determined to check whether this influence of the methoxy group also holds good for the ancestor of the methoxyfuchsone derivatives: 3-methoxyfuchsone (III).



(I)



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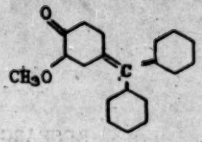


(III)

Our experiments have shown that when 3-methoxyfuchsone is heated with mineral acids, though only with concentrated ones, it is rapidly converted into a substance that is recovered as an easily fusible mass that solidifies upon cooling, is insoluble in bisulfite, and does not form the crimson-colored solutions with hydrochloric acid that are typical of 3-methoxyfuchsone. By heating the unsubstituted fuchsone with acids and then diluting the reaction mass with water we obtained the hydration product of the fuchsone – 4-hydroxytriphenylcarbinol, from which we again synthesized the initial fuchsone by dehydration.

The rate of the acid transformations of methoxyfuchsone derivatives depends essentially upon the concentration of the acid used. To explore the effect of acid concentration, we boiled dilute (0.1%) solutions of 3,3'-dimethoxybenzaurin and 3,3',-3''-trimethoxyaurin with 10%, 1%, and 0.1% hydrochloric acid, taking samples at fixed intervals of time. The research method was based upon the fact that the initial dyes form colored solutions of onium salts with a concentrated acid; the products of acid transformation are insoluble in acids. Thus the colorimetric determination of the intensity of the color of these samples when added to a definite volume of concentrated hydrochloric acid made it possible to determine the concentration of the initial substance remaining unchanged after various lengths of treatment. Our results are given in the appended table.

The results given in the table show that, with all other conditions remaining the same, 3,3'-dimethoxybenzaurin undergoes acid transformation more rapidly than 3,3',3''-trimethoxyaurin, and that lowering the strength of the acid causes a sharp drop in the rate of acid transformation, which is most marked in the case of 3,3'-dimethoxybenzaurin. A decrease in the strength of the acid has an even greater effect upon the rate of acid transformations of 3-methoxyfuchsone. In concentrated acid

TABLE

Concentration of Methoxyfuchsone Dyes after Heating with Various Concentrations of HCl

| Dye | 3,3'-Dimethoxybenzaurin | | | 3,3',3''-Trimethoxyaurin | | |
|---|---|---|---|---|---|---|
| Acid strength | 10% | 1% | 0.1% | 10% | 1% | 0.1% |
| Concentration, initial | 100 | 100 | 100 | 100 | 100 | 100 |
| Concentration after 1 hour | 10 | 70 | 100 | 70 | 95 | 100 |
| Concentration after 2 hours | 0 | 45 | 95 | 50 | 85 | 100 |
| Concentration after 4 hours | 0 | 20 | 90 | 30 | 70 | 100 |

this substance undergoes acid transformation more quickly than does 3,3'-dimethoxybenzaurin, but in 1% acid 3-methoxyfuchsone no longer undergoes the irreversible acid transformations mentioned above, but is converted into a carbinol derivative, dehydration of which yields the initial product again.

These facts lead us to conclude that methoxyfuchsone derivatives undergo acid transformations not in their fuchsone form, but in the form of the onium cation formed during dissolution in the acid and existing in equilibrium with the fuchsone form. Our researches described earlier [4] have shown that in each individual case this state of equilibrium depends both on the structure of the initial substance and on the strength of the acid. The hydroxyfuchsone dyes of aurin group, including 3,3',3''-trimethoxyaurin, form onium salts that are most resistant to hydrolysis; that is why reducing the acid strength results in a greater drop in the rate of acid transformations. The unsubstituted fuchsone and the 3-methoxyfuchsone form the least stable onium salts: they are almost totally hydrolyzed even in normal acid; that is why the drop in the acid strength makes itself most sharply felt in the acid transformations of 3-methoxyfuchsone, not taking place at all at a low acid concentration.

What is the structure of the products of the acid transformations of methoxyfuchsone derivatives? This required their isolation in a chemically pure state, which entailed extremely great difficulties over the course of a prolonged interval of time. As we have already stated, the products of the acid transformations of 3-methoxyfuchsone, 3,3'-dimethoxybenzaurin, and 3,3',3"-trimethoxyaurin are all recovered as dark, tarry curds, which harden into a brittle, brownish-yellow mass upon cooling. The latter softened in hot water and was highly soluble in most organic solvents, but the usual methods of crystallization did not result in the recovery of any individual substances. It was found that the crude products of the acid transformations of methoxyfuchsone derivatives contain small quantities of the entrained initial substances as well as low-melting impurities, whose presence, even in minute quantities, impedes the crystallization of the principal products of the acid transformations. To eliminate the initial substances, we dissolved the crude product of the acid transformations in alcohol, added sodium bisulfite, and poured the resulting solution into water. The acid-transformation product, freed of the initial substance, settled out as greenish-yellow flocs, which agglomerated in sticky clumps. Individual methods, described in detail in the experimental section, had to be found for further purification in each separate case.

The product of the acid transformations of 3-methoxyfuchsone is most easily purified. We were able to eliminate the impurities that impeded crystallization by treating the reaction product with a small quantity of ether. The bright residue left after this treatment crystallizes readily from aqueous alcohol, dilute acetic acid, or benzene. We finally recovered the principal product of the acid transformations of 3-methoxyfuchsone with a yield that approximated 60% by weight of the initial substance; it consisted of colorless acicular crystals that fused at 173-174° after first turning green; the acetyl derivative of this substance crystallized as colorless needles with a sharp m.p. of 175-176°.

Considerable difficulty was encountered in our efforts to purify the product of the acid transformations of 3,3'-dimethoxybenzaurin. The impurities that impeded crystallization were eliminated by treatment with a small quantity of 80% acetic acid. After this was done, the residue yielded to crystallization from alcohol in the presence of traces of bisulfite to protect the crystallizing substance against oxidation. We finally recovered the principal product of the acid transformations of 3,3'-dimethoxybenzaurin as colorless needles that turned yellow during desiccation by heat and fused at 199-201° after first turning green; the yield exceeded 50% by weight of the initial substance. The acetyl derivative of this substance was recovered as colorless crystalline platelets that dissolve with difficulty even in hot alcohol and fuse sharply at 227-229°.

Our greatest difficulties were encountered in isolating the pure product of the acid transformations of 3,3',3"-trimethoxyaurin. We noted that this substance

oxidizes rather rapidly and more readily than the substances described above, even during attempts to crystallize it. That is why we had to resort to repeated recrystallizations from benzene to which some glacial acetic acid and zinc dust had been added. After several crystallizations we recovered a low yield of colorless acicular crystals which turned green when heated and then fused, not sharply, at 236-240°. The acetyl derivative was synthesized as colorless crystals that fused sharply at 205-206°.

The properties and the results of analytical determinations of this substance proved it to be identical with the product of the acetylation of rubrocol, recently described by Postovsky and Kidlin [5]. Their conjectures concerning the structure of this product raises certain doubts in our minds, and we shall devote a special report to our research in this field.

Elementary analysis of the products of our acid transformations of 3-methoxyfuchsone, 3,3'-dimethoxybenzaurin, and 3,3',3"-trimethoxyaurin indicated that the empirical formulas for these transformation products were the same as those for the initial fuchsone compounds. Determination of the molecular weight of these substances and of their acetyl derivatives indicated that they were all monomers.

Determination of the methoxy groups by the Zeisel method established that the methoxy groups undergo no change during these acid transformations. Quantitative acetylation showed the acid transformations resulted in the appearance of one more phenolic hydroxyl group, which can be formed only from the carbonyl hydrogen of the initial substances.

Thus, the composition of the substances under investigation may be expressed by the following formulas:

The transformation product of 3-methoxyfuchsone – $C_{19}H_{12}(OH)(OCH_3)$,
The transformation product of 3,3'-dimethoxybenzaurin – $C_{19}H_{10}(OH)_2(OCH_3)_2$,
The transformation product of 3,3',3"-trimethoxyaurin – $C_{19}H_8(OH)_3(OCH_3)_3$.

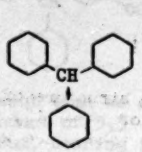
Hence the products of the acid transformations of methoxyfuchsone compounds belong to a single class, consisting of derivatives of a hydrocarbon with the formula $C_{19}H_{14}$, and differ in the number of hydroxyl and methoxy groups they have. These substances also resemble one another in their physical properties: they crystallize as colorless needles, and they all fuse after first turning green.

Thus, when 3-methoxyfuchsone, 3,3'-dimethoxybenzaurin, and 3,3',3"-trimethoxyaurin are heated with mineral acids, they undergo intramolecular transformations, resulting in the formation of isomeric compounds that are colorless and represent derivatives of a $C_{19}H_{14}$ hydrocarbon.

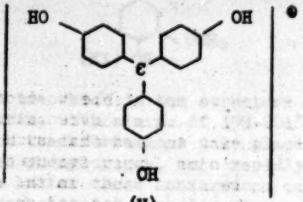
After considering the various possibilities, we came to the conclusion that this hydrocarbon must be mesophenylfluorene (IV). This hypothesis was confirmed by a study of the literature references. It was found that unsubstituted mesophenylfluorene had already been synthesized, though with low yield, from derivatives of triphenylmethane. It was synthesized by Hemilian [6], and by O. and E. Fischer [7], for instance, by heating triphenylchloromethane above 200°; similarly, Schwartz [8] synthesized mesophenylfluorene from triphenylbromomethane; Gomberg [9] found that mesophenylfluorene was formed when triphenylchloromethane was treated with phosphorus oxychloride; and, lastly, Kliegl [10] synthesized mesophenylfluorene by heating triphenylcarbinol with phosphoric acid.

In all these reactions the yield of mesophenylfluorene was low. In the reactions we investigated the closure of the mesophenylfluorene grouping ought to be facilitated by the presence of the quinonoid grouping. But the methoxy groups also exert a decisive influence. It should be remembered that when hydroxyfuchsone compounds that contain no such groups are heated with mineral acids, they do not undergo

this sort of transformation. The reason for this is that in mineral acids hydroxyfuchsone dyes give rise to mesomeric onium cations, with the structure (V) for aurin, say, in which there is no quinonoid grouping.



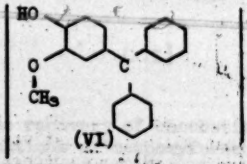
(IV)



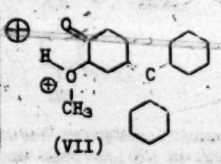
(V)

When reacted with mineral acids, the methoxyfuchsone compounds can form onium cations both from the unshared pair of electrons of the quinonoid oxygen and from the unshared pair of electrons of the methoxyl's oxygen. For instance, in the onium cation formed from 3-methoxyfuchsone structure (VI) or structure (VII) is possible. It is possible that this cation also has a hydrogen bond of type (VII).

In other words, the mesomeric cations formed from methoxyfuchsone compounds possess a quinonoid grouping to some degree. This may explain the deeper color of such cations previously noted.



(VI)



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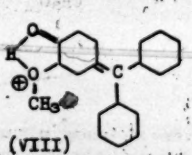
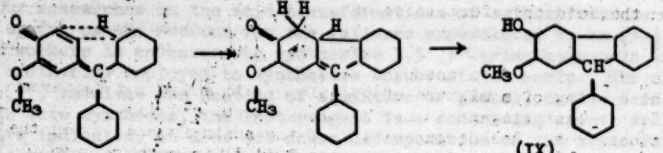


(VIII)

The presence of a quinonoid grouping imparts the high reactivity usual in quinones to methoxyfuchsone compounds in mineral acid solutions as well; this may be the reason for the ability of mesophenylfluorene to enter into intramolecular isomerization and form derivatives.

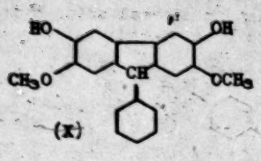
The course of such isomerization may be indicated by the following diagram (for 3-methoxyfuchsone):



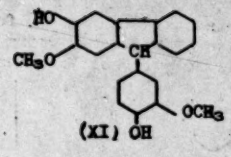
(IX)

Besides the mesophenylfluorene compound (IX) other isomeric substances, containing the methoxy group in the ortho position to the diphenyl bond, may also be formed.

Accordingly, structure (X) or (XI) may be supposed for the product of the acid transformations of 3,3'-dimethoxybenzaurin, or else substances isomeric with it, with methoxy groups in the ortho position to the diphenyl bond.



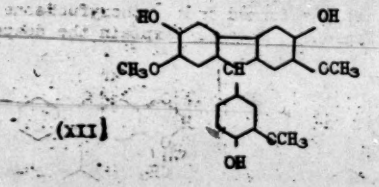
(X)



(XI)

At the present time we are unable to decide which is the structure of the acid transformation product of 3,3'-dimethoxybenzaurin, with a m.p. of 199-201°, that we have isolated. But, bearing in mind that such transformations take place with 3-methoxyfuchsone, which contains 2 unsubstituted phenyl rings, more rapidly than with 3,3'-dimethoxybenzaurin, we assume that in the latter these conversions occur more rapidly at the expense of the quinonoid and unsubstituted phenolic ring, and we therefore give preference to the structure (XI).

Correspondingly, we adopt structure (XII) for the principal product of the acid transformations of 3,3',3"-trimethoxyaurin (rubrocol). But here, too, are isomeric substances containing methoxy groups in ortho position to the diphenyl bond. It is their presence that most likely impedes the purification of these substances.



(XII)

The recovery of unsubstituted mesophenylfluorene from the products of the acid transformations of methoxyfuchsone derivatives by distilling them with zinc dust would be complete proof of their mesophenylfluorene skeleton. We have met with no success in this, and we consider the presence of the methoxy groups to be responsible. By way of comparison, we may state that when we distilled 3,3'-dimethoxy-4,4'-dihydroxytriphenylmethane with zinc dust we did not recover the unsubstituted triphenylmethane, whereas this substance was recovered without difficulty when we distilled hydroxytriphenylmethane derivatives and hydroxyfuchsone dyes that contain no methoxy groups with zinc dust.

Our researches on the acid transformations of methoxyfuchsone derivatives have cleared up for us the reasons for the failures experienced by us [11] and by other research workers in endeavors to synthesize 3,3',3"-trimethoxyaurin (rubrocol) by the methods ordinarily employed to synthesize unsubstituted aurin. The oldest of these methods [12] involves the heating of a mixture of phenol, oxalic acid, and sulfuric acid. In this synthesis, the last reagent is a condensing agent, and, as our experiments have indicated, it does not cause decomposition of the aurin formed. When the phenol is replaced by guaiacol in this condensation, the 3,3',3"-trimethoxyaurin (rubrocol) formed is acted upon by the sulfuric acid and undergoes the type of transformation mentioned above.

A newer synthesis of aurin [13] consists of condensing phenol with carbon tetrachloride in the presence of zinc chloride or aluminum chloride. When guaiacol is substituted for phenol in this condensation, the hydrochloric acid evolved during the reaction, which does not attack the aurin, causes an irreversible transformation of the 3,3',3"-trimethoxyaurin.

We are therefore able, on the basis of new experiments, to corroborate our previously expressed assertion [11] (p. 1571) that "endeavors to secure any profitable yield of rubrocol by any of the methods employed for the synthesis of aurin at high temperature and in an acid medium are doomed to failure in advance."

The failure of our effort [2] to synthesize 3,3'-dimethoxybenzaurin by the method used in the synthesis of benzaurin [13], involving the heating of a mixture of benzotrichloride and phenol, was due to the same cause. The substitution of guaiacol for phenol in this synthesis causes the liberated hydrochloric acid, which does not attack benzaurin, to bring about the transformation of the 3,3'-dimethoxybenzaurin that is formed. We recovered an easily fusible yellowish-brown mass from the reaction medium obtained by heating a mixture of benzotrichloride and guaiacol, which is like the mass obtained when known 3,3'-dimethoxybenzaurin is heated with acids.

## EXPERIMENTAL

### I. The Acid Transformations of 3-Methoxyfuchsone

A. Carrying out the reaction. Into a flask fitted with a reflux condenser there are poured 100 ml of 15% hydrochloric acid, and 10 g of 3-methoxyfuchsone is added to the heated solution. (The more accessible 3-methoxy-4-hydroxytriphenylcarbinol or bisulfite derivative of 3-methoxyfuchsone, which is converted into the hydrochloride of 3-methoxyfuchsone by heating with hydrochloric acid, may be used for this purpose). The resulting bright crimson suspension is boiled for 1-2 hours. The turning of the crimson color of the liquid to a brownish red is a sign that the acid transformations of 3-methoxyfuchsone have been completed. The 3-methoxyfuchsone is transformed into an easily fusible tarry mass, which is insoluble in strong hydrochloric acid and hardens into a dark-brown clump upon cooling. The reaction mixture is diluted with 500 ml of water, and the product of the acid transformations of 3-methoxyfuchsone is filtered out and washed with water. Weight: approximately 10 g.

The dark-brown clump thus produced contains some 3-methoxyfuchsone, although in minute quantities, entrained in the precipitation of the products of its acid transformations. To eliminate the 3-methoxyfuchsone, the reaction product is dissolved, with heating, in 50 ml of alcohol, and 2 ml of a solution of sodium bisulfite is added to the brownish-red solution formed. The solution turns yellow, and light-yellow flocs settle out when it is diluted with water. When the resulting suspension is heated, these flocs soften and agglomerate into a clump, which is removed from the solution by decantation and washed several times with hot water, decanting the solution each time. After cooling, the clump is changed into a brittle, easily pulverized mass, which is agitated in water, filtered out, washed, and dried in a vacuum exsiccator. This yields 8 g of light-yellow powder, which softens at 50-60° and fuses, not sharply, when heated to 160°.

B. Isolation and purification of the principal product of the acid transformations. 8 g of the light yellow powder prepared as above is well pulverized in a mortar and placed in a flask, and 10 ml of ether is poured over it. After standing overnight, the resulting suspension is filtered, and the deposit on the filter is washed with 1-2 ml of ether. This yields an almost colorless substance, crystalline in form, which does not soften in hot water, fuses at 150-160°, and readily undergoes further crystallization. This may be done in 50% alcohol, 50% acetic acid, or benzene. In all of these solvents we get colorless crystalline needles with a m.p. of 173-174°.

C. Properties. Colorless acicular crystals. They turn green when gradually heated above 150°. M.p. 173-174°.

The substance is moderately soluble in ether, cold benzene, alcohol, and acetic acid. It is readily soluble in these solvents when hot. It is almost insoluble in a cold aqueous alkali.

0.1305, 0.1271 g substance: 0.3995, 0.3990 g $CO_2$; 0.0688, 0.0669 g $H_2O$.
Found %: C 83.53, 83.68; H 5.84, 5.80.
$C_{20}H_{16}O_2$. Computed %: C 83.33; H 5.55.
0.1625 g substance: 0.132 g AgI.
Found %: $OCH_3$ 10.72.
$C_{19}H_{13}O(OCH_3)$. Computed %: $OCH_3$ 10.76.
0.2456, 0.2378 g substance: 8.6, 8.9 ml 0.1N NaOH (quant. acetylation).
Found %: OH 5.95, 6.12.
$C_{20}H_{15}O(OH)$. Computed %: OH 5.90.

0.3812, 0.4918 g substance: 21.47 g $C_6H_6$: $\Delta t$ 0.317°, 0.407°.
Found M: 280, 286.
$C_{20}H_{16}O_2$. Computed M: 288.

D. Acetyl derivative. 5 g of the substance is introduced into a mixture of 40 g of pyridine and 10 g of acetic anhydride and the whole is heated over a water bath for 2 hours, after which the resulting solution is poured into water. The oil that separates out hardens upon standing; the recovered product is filtered, washed with water, and dried. Yield: 5.5 g. Crystallization from 50% alcohol yields colorless crystalline needles that fuse sharply without first turning green (wherein they differ from the unacetylated substance) at 176°.

0.1237 g substance: 0.3619 g $CO_2$; 0.0645 g $H_2O$.
Found %: C 79.84; H 5.79.
$C_{22}H_{18}O_3$. Computed %: C 80.0; H 5.45.
0.3298 g substance: 21.64 g $C_6H_6$: $\Delta t$ 0.252°.
Found: M 302.
$C_{22}H_{18}O_3$. Computed: M 330.

II. Acid transformations of 3,3'-Dimethoxybenzaurin

A. Carrying out the reaction. 10 g of 3,3'-dimethoxybenzaurin hydrochloride is boiled for 6 hours with 200 ml of 10% hydrochloric acid. This causes the intensely purple solution to turn brownish-red, the initial substance converting into an easily fusible brown mass that hardens when cool. It weighs about 9 g after filtration and washing with water. To eliminate the entrained dye, the product is dissolved in 50 ml of hot alcohol, 2 ml of sodium bisulfite is added, and the yellow solution is poured into water with constant stirring. This causes a light-yellow, flocculent precipitate to settle; it is filtered out, washed well with water, dried in a vacuum exsiccator. Product softens in cold water, melts, not sharply, over range of 60-150°. Yield: approx. 7 g.

B. Isolation and purification of the principal product of the acid transformations. The easily fusible product described above is dissolved by heating with 20 ml of 50% acetic acid. After prolonged standing, a light-yellow deposit separates; it is filtered out, pressed out well, washed with hot water, and dried. Resulting crystalline substance weighs 5 g, fuses at 160-170°, and can be readily recrystallized from alcohol and acetic acid. With traces of bisulfite present, we recover colorless crystals that turn slightly yellow when dried by heat, green when heated to 160-170°, fuse at 199-201°.

C. Properties. Colorless, beautifully shaped needles. Less soluble in ether than the product of the acid transformations of 3-methoxyfuchsone; soluble in alcohol, acetic acid, and benzene; soluble in an aqueous alkali, forming a colorless solution that turns yellow upon standing.

0.1212 g, 0.1517 g substance: 0.3343 g, 0.4181 g $CO_2$; 0.0564 g, 0.0730 g $H_2O$.
Found %: C 75.22, 75.16; H 5.21, 5.38.
$C_{21}H_{18}O_4$. Computed %: C 75.45; H 5.35.

0.1709 g substance: 0.2347 AgI.
Found %: $OCH_3$ 18.04.
$C_{19}H_{12}O_2(OCH_3)_2$. Computed %: $OCH_3$ 18.56.

0.2384 g, 0.2710 g substance: 14.0 ml, 15.6 ml 0.1N NaOH (quantitative acetylation)
Found %: OH 9.98, 9.79.
$C_{21}H_{18}O_2(OH)_2$. Computed %: OH 10.18.

0.1952 g substance: 32.38 g $C_6H_6$: $\Delta t$ 0.098°.
Found: M 308.
$C_{21}H_{18}O_4$. Computed: M 334.

D. Acetyl derivative. 1) Synthesis from the product of the acid transformations of 3,3'-dimethoxybenzaurin. 5 g of the substance with a m.p. of 199-201° is placed in a mixture of 40 g of pyridine and 10 g of acetic anhydride, and the resulting solution is heated for 2 hours over a water bath. The crystals of the acetylation product, only slightly soluble in organic solvents, begin to settle out of the solution during this heating process; as the reaction mass cools, the amount of these crystals increases. After dilution with water, the precipitate is filtered out, washed well, dried, and recrystallized from alcohol or glacial acetic acid. The substance is hardly soluble even in hot alcohol. It is best to crystallize it from glacial acetic acid. Recrystallization yields the diacetyl derivative as colorless crystalline lamellae with a sharp m.p. of 227-229°.

0.1265 g substance: 0.3519 g $CO_2$; 0.0622 g $H_2O$.
Found %: C 71.65; H 5.46.
$C_{25}H_{22}O_6$. Computed %: C 71.72; H 5.24.

2) Synthesis by the direct acetylation of 3,3'-dimethoxybenzaurin. 3 g of anhydrous 3,3'-dimethoxybenzaurin hydrochloride is added to a mixture of 20 g of acetic anhydride and 20 g of acetyl chloride. The solution is crimson at first, but turns yellow when heated. After boiling for 2 hours over a water bath, the resulting solution is poured into water. The resulting colorless precipitate is heated with 20 ml of alcohol. This causes part of the precipitate to enter solution, but the bulk of it, approximately 3 g, does not dissolve. When hydrochloric acid is added to the filtered solution, the latter turns crimson, which indicates the presence of the normal acetyl derivative of 3,3'-dimethoxybenzaurin. The precipitate that did not dissolve in alcohol is not colored by hydrochloric acid; after recrystallization from large quantities of alcohol or from glacial acetic acid, it is recovered as colorless crystals with a m.p. of 227-229°, which exhibit no depression when mixed with the acetyl derivative of the product of the acid transformations of 3,3'-dimethoxybenzaurin described above.

## III. Acid Transformations of 3,3',3"-Trimethoxyaurin.

10 g of 3,3',3"-trimethoxyaurin hydrochloride is added to 200 ml of 10% hydrochloric acid, and the resulting suspension is boiled for 2 to 3 days. The precipitate, which is crystalline at first, gradually changes, turning into a sticky clump after two days have passed; the solution remains crimson-purple in color. The precipitate is filtered out from the solution and dissolved by heating it in 100 ml of alcohol. 5 ml of a saturated solution of bisulfite is added to the resulting red solution, which turns yellow and is then poured into 1 liter of water. The resulting brownish yellow precipitate is filtered out, washed with water, and dried. Yield: 5-6 g. The dried precipitate is dissolved by heating it in 200 ml of benzene, 1 ml of glacial acetic acid and 5 g of zinc dust are added to the solution, and - after it has been boiled for 2 hours - the light-yellow solution is filtered and then evaporated down to 50 mg. The tarry impurities that separate out are removed by filtration, and the hot solution is quickly cooled to 30-40° with constant stirring. This causes a light-

yellow precipitate to settle, which is filtered out before the solution has completely cooled. Repeated recrystallization from alcohol yields a colorless crystalline precipitate, which turns green when heated above 150° and fuses, not sharply, at 236-240°. The product yield varies from 0.5 to 1.5 g, depending on how crystallization is carried out.

Acetylation with a mixture of acetic anhydride and pyridine yielded an acetyl derivative that fused at 204-206° after crystallization from alcohol.

## SUMMARY

When fuchsone derivatives that contain methoxy groups in the ortho position to the oxo group are heated with mineral acids, they undergo irreversible specific acid transformations. The principal products of such transformations are colorless substances that have the same empirical formulas and molecular weights as the initial substances.

The research results indicate that this isomerization of methoxyfuchsone derivatives involves the closure of the mesophenylfluorene grouping.

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# RESEARCH ON THE THERMAL STABILITY AND VOLATILITY OF NORMAL WOLFRAMATES OF THE ALKALI ELEMENTS

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The author has shown [1] that the normal wolframates of rubidium and caesium are partially decomposed at temperatures above 900-950°. The oxide of the alkali element that is liberated is vaporized, the calcination residue being enriched with wolfram trioxide. These wolframates can also be vaporized directly. Both of these processes are intensified as the temperature rises above 1200°, this being especially true of vaporization.

It was the object of the present research to determine the thermal stability and the volatility of the normal wolframates of all the alkali elements under comparable conditions.

There is almost no information available on the volatility of alkali wolframates. In his study of the action of hydrogen on potassium wolframate, van Liempt [2] found that this compound vaporizes completely at 1050°.

The literature sheds no light on the thermal stability of the normal wolframates of lithium, sodium, and potassium.

The initial preparations of normal lithium and potassium wolframates were prepared by fusing calculated quantities of the respective alkali carbonate with wolframate trioxide. Normal sodium wolframate was recovered from a solution produced by the action of a slight excess of sodium hydroxide upon wolframic acid, and, after double recrystallization, it was dehydrated by calcining it to the melting point. The rubidium and caesium wolframates were prepared by fusing silver wolframate with the respective alkali chloride, as described in the paper cited above [1]. The analyses of all these preparations are given in table 1.

It has been established in preliminary tests that lithium and sodium wolframates suffer only a slight change in weight up to as high as 1200° (about 1 mg when a weighed quantity of some 0.25 g was calcined for 6 hours). Potassium wolframate exhibited a loss of weight after being heated to 1000° for 2 hours. This loss of weight is found in rubidium wolframate in the 950-1000° range, while caesium wolframate is volatile and unstable at temperatures above 900°.

To compare the volatility and thermal stability of the normal wolframates of the alkali elements, weighed batches of about 0.2-0.3 g were calcined for 6 hours at a temperature of 1200° in open platinum crucibles placed in an electric furnace. The lithium and sodium wolframates were heated for 24 to 48 hours to obtain a noticeable loss of weight. The experimental results are listed in Table 2. Analysis of the

TABLE 1

Initial Preparations of the Normal Wolframates of the Alkali Elements

(The preparations were analyzed by the mercuronitrate method)

| Compound | Preparation no. | Per cent of $WO_3$ | |
|---|---|---|---|
| | | Found | Computed |
| $Li_2WO_4$ | 1 | 88.75 | 88.59 |
| $Na_2WO_4$ | 1 | 79.01 | 78.91 |
| $K_2WO_4$ | 1 | 71.73 | 71.13 |
| | 2 | 71.12 | 71.13 |
| $Rb_2WO_4$ | 1 | 56.41 | 55.39 |
| | 2 | 56.15 | 55.39 |
| $Cs_2WO_4$ | 1 | 45.11 | 45.15 |

ercent of $WO_3$ in the residue, compared to the observed loss of weight during calcination, enabled us to compute the degree of decomposition and the extent of the volatilization of the compounds, based in all cases on a 6-hour period. Data on the volatility of wolfram trioxide are also listed for the sake of comparison with the wolframates.

The mean values of the degree of decomposition and the rate of vaporization of the normal wolframates of the alkali elements, computed from the data of Table 2, are listed in Table 3.

The normal wolframates of all the alkali elements are thermally unstable and vaporizable at 1200°, some of them being unstable at even lower temperatures. These two phenomena may be related, and in some of the wolframates, or partially in all of them, the process of vaporization of the salt consists of the volatilization of equivalent quantities of wolfram trioxide and the oxide of the alkali element, produced by the thermal dissociation of the wolframate. Both wolfram trioxide and the oxides of the alkali elements are quite volatile at the temperatures at which these tests were made. There is no doubt, however, that the wolframates also vaporize directly. This is seen, for instance, in the fact that the relative volatility of caesium wolframate exceeds the volatility of wolfram trioxide.

The thermal decomposition of normal wolframates takes place as follows:

$$Me_2WO_4 \rightleftharpoons MeO + WO_3.$$

It may be that the alkali elements with high atomic numbers then form peroxides with atmospheric oxygen.

All the wolframates we have investigated, without exception, exhibit an increase in the percent of wolfram trioxide in the calcination residue. Thus, for the decomposition products of normal wolframates, it is principally the oxide of the alkali element that vaporizes, the wolfram trioxide being wholly or partially dissolved in the residue of the salt, constituting an polywolframate impurity in it.

In lithium and sodium wolframates, the degree of decomposition exceeds the extent of vaporization (expressed in per cent of the initial weight). In potassium, rubidium, and caesium wolframates, the degree of decomposition is many times less than the vaporization.

TABLE 2

Calcination of Normal Wolframates of the Alkali Elements at 1200°

| Compound | Test No. | Calcination time (hours) | Initial weight (g) | % of $WO_3$ in the preparation | | Loss of weight | | Loss of weight, based on 6 hours of calcination (%) | Transformation of the preparation in 6 hours | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | before test | after test | (g) | (%) | | decomp. (%) | Vaporization (%) | Vaporization millimols |
| $Li_2WO_4$... | 1 | 24 | 0.2592 | 88.75 | 89.13 | 0.0043 | 1.67 | 0.42 | 0.93 | 0.31 | 0.003 |
| | 2 | 24 | 0.2510 | 88.75 | 89.78 | 0.0044 | 1.75 | 0.44 | 2.88 | 0.15 | 0.001 |
| $Na_2WO_4$... | 1 | 36 | 0.2719 | 79.01 | 79.66 | 0.0049 | 1.80 | 0.30 | 0.64 | 0.16 | 0.001 |
| | 2 | 48 | 0.2638 | 79.01 | 79.84 | 0.0042 | 1.59 | 0.20 | 0.54 | 0.08 | 0.001 |
| $K_2WO_4$.... | 1 | 6 | 0.2672 | 71.73 | 71.96 | 0.0072 | 2.69 | 2.69 | 0.91 | 2.42 | 0.020 |
| | 2 | 12 | 0.2784 | 71.12 | 71.82 | 0.0144 | 5.17 | 2.58 | 0.69 | 2.45 | 0.021 |
| | 3 | 6 | 0.3226 | 71.73 | 72.04 | 0.0072 | 2.19 | 2.19 | 1.18 | 1.87 | 0.019 |
| $Rb_2WO_4$... | 1 | 6 | 0.2449 | 58.41 | 59.19 | 0.0141 | 5.76 | 5.76 | 2.87 | 4.87 | 0.027 |
| | 2 | 7.5 | 0.2325 | 56.15 | 57.26 | 0.0219 | 9.21 | 7.37 | 3.97 | 7.37 | 0.033 |
| | 3 | 8 | 0.5089 | 56.41 | 56.85 | 0.0272 | 5.35 | 4.02 | 1.12 | 3.61 | 0.043 |
| $Cs_2WO_4$ | 1 | 6 | 0.2618 | 45.11 | 45.48 | 0.0585 | 22.35 | 22.35 | 4.32 | 19.97 | 0.102 |
| | 2 | 4 | 0.2381 | 45.11 | 45.68 | 0.0538 | 22.60 | 33.90 | 2.76 | 32.38 | 0.150 |
| $WO_3$... | 1 | 6 | 0.2210 | - | - | 0.0415 | 15.82 | 15.82 | - | 15.82 | 0.179 |

TABLE 3

Degree of Decomposition and Volatility of Normal Wolframates of the Alkali Elements at 1200°

(Calcination time: 6 hours. Initial weight: approx. 0.25 g).

| Compound | Mean loss of weight, % | Degree of decomposition, % | Rate of vaporization | |
|---|---|---|---|---|
| | | | In percent of initial weight | In millimols |
| $Li_2WO_4$ ..... | 0.43 | 1.73 | 0.25 | 0.002 |
| $Na_2WO_4$ ..... | 0.25 | 0.59 | 0.12 | 0.001 |
| $K_2WO_4$ ..... | 2.49 | 0.86 | 2.25 | 0.020 |
| $Rb_2WO_4$ ..... | 5.72 | 2.35 | 5.35 | 0.034 |
| $Cs_2WO_4$ ..... | 28.12 | 3.54 | 26.17 | 0.126 |
| $WO_3$ ..... | 15.82 | - | 15.82 | 0.179 |

The minimum volatility and the maximum thermal stability are exhibited by sodium wolframate. The thermal stability of the normal wolframates of the alkali elements diminishes uninterruptedly while the vaporizability increases. Lithium wolframate is also less stable and more volatile than sodium wolframate.

The instability of alkali wolframates at high temperatures may be due to several causes.

In the case of lithium and sodium wolframates we evidently observe the well-known phenomenon of counterpolarization. At high temperatures, the lithium ion, whose radius is the smallest of all the alkali-elements' ions, polarizes the oxygen ions in the $WO_4^{-2}$ anion, thus facilitating the decomposition of the wolframate into the corresponding oxides. Sodium wolframate is more stable owing to the lower polarizing action of the sodium ion.

The decrease in thermal stability again observed as we pass to the wolframates of potassium, rubidium, and caesium, cannot be explained by counterpolarization, inasmuch as the polarizing effect of the ions of the alkali elements diminishes as we proceed along the series.

The observed thermal instability of potassium wolframate confirms the view previously expressed by the author [1] concerning the reasons for the decomposition of rubidium and caesium wolframates during calcination. In the anion of wolframic acid, $WO_4^{-2}$, the rather large effective radius of the hexavalent wolfram atom (approximately 0.5 A) does not enable it to polarize the oxygen ions enough to make the anion "monolithic." We know that the closest lower analog to wolfram - uranium - is an amphoteric element, and that two oxygen ions are readily detached from the $UO_4^{-2}$ radical by acids, resulting in the formation of the uranyl ion, $UO_2^{+2}$.

For these reasons, the oxygen ions in the $WO_4^{-2}$ anion can apparently exert their own polarizing action upon the bulky cations of the alkali elements potassium, rubidium, and caesium. We call this phenomenon "selective polarizing action" to distinguish it from the polarizing action of the $WO_4^{-2}$ ion as a whole, which must be very slight owing to the large effective radius of this ion (approximately 3.50 A).

The selective polarizing action of the oxygen ions in the $WO_4^{-2}$ radical tends to strengthen the bond between the oxygen and the ions of the alkali elements, conferring a polar quality upon it, and weaken the bond between the oxygen and wolfram atoms. The intensification of all these processes at high temperatures tends to result in detaching an oxide of the alkali element and in considerable volatility of the compounds.

This ought to happen most easily in caesium compounds, inasmuch as the caesium ion has the largest effective radius of all the known alkali elements and is polarized more than the others. As we pass to the upper representatives of the group of alkali elements - rubidium, potassium, and sodium - the phenomenon of polarization in the wolframate molecules tends to grow weaker, with the stability of the compounds rising accordingly.

As the "monolithic nature" of the anion increases, the selective polarizing action of the oxygen ions that comprise it tends to weaken. This is why normal sulfates of potassium, rubidium, and caesium sulfates are stable at 1200°, as Victor I. Spitsyn and V.I.Shostak have shown [3]. It is to be expected that the silicates of these elements will be less stable, inasmuch as the $Si^{+4}$ atom exhibits a lower polarizing action that $S^{+6}$, and hence the $SiO_2^{-2}$ ion is less "monolithic" than the $SO_4^{-2}$ ion.

## SUMMARY

1. The thermal stability and the volatility of the normal wolframates of the alkali elements have been investigated.

The onset of a noticeable loss of weight of the wolframates due to vaporization and partial decomposition is observed at the following temperatures:

| $LiWO_4$ | $Na_2WO_4$ | $K_2WO_4$ | $Rb_2WO_4$ | $Cs_2WO_4$ |
|---|---|---|---|---|
| 1200° | 1200° | 1000° | 950° | 900° |

2. Decomposition of all these wolframates is accompanied by detachment of an oxide of the alkali element. Under comparable conditions (1200°, 6 hours of calcination), the degree of decomposition, in per cent, is:

| $Li_2WO_4$ | $Na_2WO_4$ | $K_2WO_4$ | $Rb_2WO_4$ | $Cs_2WO_4$ |
|---|---|---|---|---|
| 1.73 | 0.59 | 0.86 | 2.39 | 3.54 |

3. The thermal instability of lithium and sodium wolframates and the pattern of its variation are related to the phenomenon of counterpolarization.

4. The thermal instability of potassium, rubidium, and caesium wolframates is due to the "selective polarizing action" of the oxygen ions in the wolframic acid anions upon the ions of the alkali elements. This phenomenon is intensified as we pass from potassium to caesium, with an increase in the ion radii and in the polarizability of the cations.

5. The rate of vaporization of alkali wolframates varies in the same way as the degree of their decomposition. Caesium wolframate is most volatile.

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# ATOMIC WEIGHT AS A FUNCTION OF A SERIES OF INTEGERS

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In his review of existing attempts to express atomic weight as an exact function, Dmitri Ivanovich Mendeleyev [1] stated that the most successful of these efforts was that of Vincent, who expressed atomic weights by the equation:

$$W = N^{1.2}$$

where W is the atomic weight, and N represents a series of integers from N = 1 for hydrogen to N = 92 for uranium.

The higher the atomic weight of an element, the greater the accuracy of this equation, while the lower the element's atomic weight the less its accuracy. For example: according to this equation the atomic weight of uranium is 238, which is its actual atomic weight; but the equation gives the atomic weight of lithium as 3.8, whereas it actually is 6.94.

To express atomic weights with uniformly satisfactory accuracy for all elements, the following equation may be assumed, differing from Vincent's equation:

$$W = (2 + N)^{1.2},$$

where W and N, denote the atomic weight and a series of integers, respectively, as in Vincent's equation.

The accuracy of this newer equation for all the elements, beginning with lithium and ending with uranium is the same as that of Vincent's equation for uranium and elements of comparable atomic weights. The foregoing is illustrated by the subjoined table, showing the atomic weights of several elements: their actual weights being listed together with their weights as computed by our equation and by Vincent's equation.

TABLE

| Element | N | W (actual) | $W = (2 + N)^{1.2}$ | $W = N^{1.2}$ |
|---|---|---|---|---|
| Li ..... | 3 | 6.94 | 6.94 | 3.8 |
| Be ..... | 4 | 9.02 | 8.6 | 5.35 |
| B ..... | 5 | 10.82 | 10.8 | 7 |
| C ..... | 6 | 12.00 | 12 | 8.8 |
| N ..... | 7 | 14.008 | 14 | 10.5 |
| O ..... | 8 | 16.000 | 16 | 12.5 |
| F ..... | 9 | 19.00 | 18 | 14.3 |
| Au ..... | 79 | 197.2 | 197 | 198 |
| Hg ..... | 80 | 200.06 | 200 | 200 |
| | 81 | 204.4 | 201 | 201 |
| Pb..... | 82 | 207.2 | 204 | 205 |
| Bi..... | 83 | 209 | 208 | 210 |
| Po..... | 84 | 210 | 210 | 212 |

This table indicates that our equation provides a more accurate expression for the atomic weight than does Vincent's equation.

Our equation does not give the atomic weight of hydrogen or of helium.

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